Model development of ionic-strength-sensitive hydrogel and finite element analysis of gel and dielectrics

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MODEL DEVELOPMENT OF IONIC-STRENGTH-SENSITIVE HYDROGEL
AND
FINITE ELEMENT ANALYSIS OF GEL AND DIELECTRICS

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Summary

As one of the most important smart hydrogels, the ionic-strength-sensitive hydrogel is increasingly attracting the attention of academic researchers and industrial engineers, due to the wide-range applications in the areas of drug delivery, artificial organ, biomicroelectromechanical (BioMEMS) and so on, resulting from the excellent characteristics, such as controllable swelling/shrinking, sorption capacity, reversible large deformation, good permeability and surface property. So far numerous experimental studies have been carried out for the understanding of the characteristics and mechanism of the ionic-strength-sensitive hydrogel. However, few efforts have been made on the theoretical model development and numerical simulation.

In this thesis, a chemo-electro-mechanical model is developed theoretically for simulation of the deformation and chemical as well as electric characteristics of the ionic-strength-sensitive hydrogel, which is termed the Multi-Effect-Coupling Ionic-Strength-Stimulus (MECis) model. The model is capable of modeling the chemical, electric and mechanical fields, where the three sets of the field equations govern the mass conservation, the electric field and the momentum conservation in both the hydrogel and solution domains. Associated with the field governing equations, the three sets of the constitutive laws are also formulated, namely the constitutive flux, the fixed charge equation, and the mechanical material law. In particular, the developed constitutive laws describe how the smart hydrogel responds to the change of the ionic strength of the solution, by considering the significant influence of the ionic strength on the ionic flux, the equilibrium reaction between the fixed charges and mobile ions, and the charge-to-charge repulsive force.

An equilibrium analysis of the ionic-strength-sensitive hydrogel is then conducted by the steady-state MECis simulation, where the equilibrium swelling and shrinking of various ionic-strength-sensitive hydrogels are investigated firstly, in order to validate the presently developed model. The simulation results are compared with the corresponding experiments, and good agreement is achieved qualitatively and

quantitatively. Further, the steady-state MECis model is also compared with the modified Flory-Rehner theory-I and -II, as well as the gel-swelling model. It is demonstrated that the present MECis model can work more accurately by considering more physical and chemical environmental conditions. In addition, the four parameter studies are carried out, in order to understand how the physical and chemical parameters affect the equilibrium characteristics of the ionic-strength-sensitive hydrogel, including the influences of the initial fixed charge density, the equilibrium constant, the Young's modulus, and the initial fixed charge distance on the equilibrium characteristics. The influence of these parameters is presented in terms of the swelling ratio, the chemical, electric and mechanical fields, where the distributions of several important field variables are analyzed in details, such as the fixed charge density, the ionic concentration, the electric potential, and the displacement.

Apart from that, the kinetics of the ionic-strength-sensitive hydrogel is also analyzed by the transient MECis simulation, where the present model is employed first to investigate the kinetics of the swelling/shrinking and/or reversible properties of various ionic-strength-sensitive hydrogels, and then compared with the corresponding experiments. The comparisons show that the MECis model is capable of modeling and simulating of the kinetic characteristics of the ionic-strength-sensitive hydrogels accurately. The influence of the chemical and physical parameters is then studied systematically on the kinetic swelling/shrinking of the ionic-strength-sensitive hydrogel, where the reversible kinetics and the influences of the initial fixed charge density and Young's modulus on the kinetics of the hydrogel are discussed in details. The kinetics of the swelling ratio with different parameters, and the kinetic distributions of the significant field variables are analyzed as well, including the fixed charge density, the ionic concentration, the electric potential, and the displacement.

Finally, the finite element methods are implemented for the investigation of the kinetic deformation of the gels in water and the equilibrium of dielectrics, respectively. Firstly, the kinetic deformation patterns of the gels with various shapes and constraints in water are analyzed by the finite element model, including the constrained, the block, the thin film, and the bonded gels, where different deformation patterns are achieved, such as the buckling, twisting, wrinkling, folding, and waving. The experiments are also carried out to observe the swelling and wrinkling of the cubic and thin film gels. The simulation is compared with the experiments and a good agreement is observed. Then the finite element formulation is developed for the dielectrics, based on an

existing field theory. The formulation is employed to analyze the deformation of the dielectric gels subject to the electromechanical load without and within the solvent, where the simulation results are compared with the analytical solution, and a very good agreement is achieved.

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Glossary

1D, 2D, 3D	One, two, three dimension
$B_i, \mathbf{B}$	Body force
C^f	Fixed charge density
C_0^f	Fixed charge density in the reference configuration
$C_{s,0}^f$	Initial fixed charge density in the dry state of hydrogels
c^k	True concentration of the k th species
C^k	Nominal concentration of the k th species
$C_{ij}, \mathbf{C}$	Cauchy-Green stress tensor
d	Diameter of hydrogels
$\det \mathbf{F}$	Determinant of the deformation gradient
D^a	Diffusion coefficient of the a th species
$D_i, \mathbf{D}$	True electric displacement
$dS(\mathbf{X})$	Surface of the control volume around particle $\mathbf{X}$
$\tilde{D}_i, \tilde{\mathbf{D}}$	Nominal electric displacement
ESR	Equilibrium swelling ratio
E	Young's modulus
$E_{ij}, \mathbf{E}$	Green-Lagrange strain tensor
$E_i^f, \mathbf{E}^f$	True electric field
$\tilde{E}_i^f, \tilde{\mathbf{E}}^f$	Nominal electric field
FEM	Finite element method
F	Faraday constant
$F_{ij}, \mathbf{F}$	Deformation gradient tensor
G	Free energy of a system

H	Hydration of the hydrogel
$H_{ij}, \mathbf{H}$	Inversion of deformation gradient tensor $F_{ij}, \mathbf{F}$
i	Molecule flux on a surface
I	True ionic strength
$\tilde{I}$	Nominal ionic strength
$j_i^k, \mathbf{j}^k$	Flux of the k th species
$J_i^k, \mathbf{J}^k$	Nominal flux of k th species
kT	Temperature in energy form
K	True dissociation constant
$\tilde{K}$	Nominal dissociation constant
K_0	True intrinsic dissociation constant
$\tilde{K}_0$	Nominal intrinsic dissociation constant
l, m	Lamé's coefficients
MECis	Multi-effect-coupling ionic-strength-stimulus
$M_{ij}^a, \mathbf{M}^a$	Mobility tensor of the a th species
$N_a, \mathbf{N}$	Shape functions
N_A	Avogadro's constant
$P_{ij}, \mathbf{P}$	Nominal stress or the first Piola-Kirchhoff stress tensor
q	Elementary charge
$Q(\mathbf{X}, t)$	Charge density in a volume
r	Distance between fixed charges
r^a	Generation rate of a th particle in the control volume
R	Gas constant
$ \mathbf{R} $	Distance between two charges in the reference configuration
$S_{ij}, \mathbf{S}$	Second Piola-Kirchhoff stress tensor
SR	Swelling ratio
t	Time
T	Absolute temperature
$T_i, \mathbf{T}$	Traction force

$u_i, \mathbf{u}$	Displacement
v	Volume of per solvent molecule
$\mathbf{v}, v_i$	Velocity field
w	Iterative solution of the systems of equations
$W, \tilde{W}$	Free energy function of the hydrogel
z_a	Valence of the a th species
z_f	Valence of the fixed charges
z^k	Valence of the k th ionic species
γ^k	Chemical activity coefficient
δ_{ij}	Kronecker delta function
ε	Permittivity of the materials
ζ, ξ_i	Test functions
η^a	Electric mobility of the a th species
θ	Dimensionless parameter
κ	Debye shielding length
λ_i	Stretching ratio in the i th direction
μ^k	Chemical potential of the k th species
ν	Poisson's ratio
π^a, Π^a	The a th type of osmotic pressure
ρ	Density
$\sigma_{ij}, \boldsymbol{\sigma}$	Cauchy stress tensor
ϕ^i	Volume fraction of i th species
χ	Dimensionless material parameter
ψ	Electric potential
ω	Electrostatic potential of an elementary charge
Ω	Charge density on a surface

1

Introduction

1.1. Background

1.1.1. Hydrogel and Application

Hydrogel is a class of hydrophilic crosslinked polymeric networks with three phases, namely, the three-dimensional polymeric network solid matrix, interstitial fluid, and ionic species. The three-dimensional solid matrix network is formed by the crosslinked polymeric chains with physical or chemical bonds, for example, the covalent bond, hydrogen bond, van der Waals interaction, and entanglement (Kamath and Park, 1993; Peppas *et al.*, 2000). These elastic polymeric networks furnish the structural and physical integrity of the hydrogel, which guarantees the hydrogel exhibit a thermodynamic compatibility with fluid, and allows the hydrogel to swell or shrink in the aqueous media (Flory and Rehner, 1943a, b). The interstitial fluid fills up the interstitial space within the networks, and it may be composed of hydrated, interfacial or bulk fluid (Jhon and Andrade, 1973), which determines the overall permeation of the substance into and out of the gel (Hoffman, 2002). The ionic species consist of mobile ions in the interstitial fluid and the ionic monomers bound on the polymeric chains and play a significant role in the responsive characteristics of the hydrogel to external stimuli of the environmental solution (Tanaka *et al.*, 1980). Due to the designed structure, the hydrogel, also known as elastomer, possesses both solid and liquid properties, and is capable of undergoing large reversible deformation by imbibing a large amount of water or biological fluid (Hong *et al.*, 2008; Osada and Gong, 1993; Tanaka, 1981).

There are several classifications of hydrogels, depending on their properties and applications. For example, they can be amorphous, semi-crystalline or hydrogen bonded hydrogel according to their structural characteristics. They can also be

homopolymeric, copolymeric or multipolymeric, based on the method of preparation and synthesis (Peppas *et al.*, 2000). Drug release from hydrogels can be diffusion controlled, swelling controlled, chemical controlled, or environmental responsive systems. The hydrogels can also be neutral, anionic, cationic, and ampholytic due to the different pendant groups on the polymeric chains. Anionic, cationic and ampholytic hydrogels are also known as ionic, ionized or polyelectrolyte hydrogels.

There is a class of polyelectrolyte hydrogels which are capable of responding to the environmental stimuli. They have been attracting much attention since the pioneering work of Tanaka (1978; 1981). Such hydrogels are known as smart, intelligent, stimuli-responsive or environmentally sensitive hydrogels. Smart hydrogels might identify an external environmental stimulus change as a signal, and then change the chain conformation in direct response via undergoing discrete or continuous volume phase transition. Various environmental stimuli may modulate the response of smart hydrogels, which are categorized either chemically or physically. Chemical stimuli include solution pH (Brannon-Peppas and Peppas, 1991a; Marandi *et al.*, 2008; Siegel and Firestone, 1988), glucose concentration (Hassan *et al.*, 1997; Lee *et al.*, 2004; Schwartz *et al.*, 1998), solvent composition (Tanaka *et al.*, 1980), and ionic strength (Caykara and Dogmus, 2005; Hooper *et al.*, 1990; Markland *et al.*, 1999; Zhao and Moore, 2001). Physical stimuli include environmental temperature (Gottlieb *et al.*, 2007; Tanaka, 1978, 1979), electric field (Tanaka *et al.*, 1982), and light/photon (Irie, 1986; Irie and Kunwatchakun, 1986). In addition, there are also smart hydrogels which may respond to multiple coupled stimuli, such as the pH-temperature-sensitive hydrogel (Khurma and Nand, 2008; Kim *et al.*, 2002; Lee and Shieh, 1999; Park *et al.*, 2007), the pH-thermo-ionic-strength-sensitive hydrogel (Jun Yang, 2007), the pH-ionic-strength-sensitive hydrogel (Markland *et al.*, 1999), and the electric-pH-sensitive hydrogel (Kim *et al.*, 2004).

Smart hydrogels have been used in many bioengineering applications, due to their unique properties including their swelling/shrinking behavior, sorption capacity, mechanical property, permeability, and surface property. For instance, the hydrogel can be used for microfluidic control (Eddington and Beebe, 2004), sensor/actuator (Guenther *et al.*, 2008; Huck, 2008) and in separation processes (Andrews, 1986), as artificial muscles (Shahinpoor, 1994), in cell engineering (Hynd *et al.*, 2007; Jen *et al.*, 1996), and in chemical engineering (Linden *et al.*, 2003; Osada and Gong, 1993). Smart hydrogels also have extensive applications in the medical and pharmaceutical

fields, such as the drug delivery system (Hoare and Kohane, 2008; Huang *et al.*, 2007; Kim *et al.*, 1992; Qiu and Park, 2001), tissue engineering (Biancamaria, 2007; Lee and Mooney, 2001; Studenovská *et al.*, 2008), artificial organ (Li *et al.*, 2006b; Sawa *et al.*, 2008), and wound dressing (Jones and Vaughan, 2005; Snyders *et al.*, 2007; Yoo and Kim, 2008).

1.1.2. Ionic-Strength-Sensitive Hydrogel

The ionic-strength-sensitive hydrogel is a special type of smart hydrogels, which is able to respond to the change in the ionic strength of surrounding solutions. In general, the ionic strength is defined as the concentration of dissolved ions in a solution by $I = 0.5 \sum z_k^2 c_k$, where z_k and c_k are the valence and concentration of the k th ionic species, respectively. It is one of the main characteristics of an electrolyte solution and may affect important properties of the solution, such as its dissociation or the solubility of different salts in the solution. Among all the environmental stimuli, the ionic strength is one of the most important since most hydrogel-based applications require a solution in which the gel is immersed.

There are two types of the ionic-strength-sensitive hydrogels, namely, the weakly and strongly dissociable polyelectrolyte gels. Usually they are synthesized by incorporating different ionic monomers, for example, the weak monomers which partially dissociate in the solution, such as acrylic acid (AA) and maleic acid (MA) (Liu *et al.*, 2007; Wu *et al.*, 2006; Zhao and Moore, 2001), and the strong monomers which completely dissociate in the solution, such as [(methacrylamido)propyl]-trimethyl-ammonium chloride (MAPTAC), and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) (Baker *et al.*, 1994; Hooper *et al.*, 1990; Okay *et al.*, 1998).

The ionizable groups in the ionic-strength-sensitive hydrogel may dissociate partially or completely in the solution for both weak and strong electrolyte, respectively. After dissociation, the charged groups are left on the polymeric chains, and they are well known as the fixed charge groups. When a hydrogel is immersed in a solution with electrolytes, the fixed charge groups may be bonded by mobile counterions in the solution and thus affect the swelling/shrinking behavior of the hydrogel. The weakly and strongly dissociable ionic-strength-sensitive hydrogels may have different directions of the bound reaction between the fixed charge groups and

the counterions. In addition, the electrostatic repulsive forces among the fixed charges may also contribute to the deformation of hydrogel (Qiu and Park, 2001). Therefore, the fixed charge density plays a significant role in the swelling or shrinking behavior of the ionic-strength-sensitive hydrogel.

1.2. Literature Review

1.2.1. Theoretical Models for Hydrogel

In order to elucidate the characteristics of the hydrogel, a variety of theoretical frameworks from different interests were developed to predict their deformation behavior, degree of ionization, diffusive mechanism of the mobile ion, polymer-solvent interaction and so on. In this section, several theories and models are reviewed at the level of macro-, meso- and micro-scales, respectively.

- The theoretical models at macro-scale level predict the macro continuous behavior of the hydrogel, including the macroscopic continuum model, the mixture theory, the kinetic theory, and the constitutive model, as reviewed in Subsections 1.2.1.1 to 1.2.1.4, respectively;
- The meso-scale theories are used to study the characteristics of hydrogels at the scale between the macro- and micro-scale levels. They include the Flory-Huggins theory, Flory-Rehner theory and the corresponding extension, and the lattice model, as commented in Subsections 1.2.1.5 to 1.2.1.8, respectively;
- The theories at micro-scale level focus on the characteristics of molecular or ionic particles to evaluate the properties of the hydrogel. They include molecular dynamics, Monte Carlo simulation, and other microscopic theories, as discussed in Subsections 1.2.1.9 to 1.2.1.11, respectively.

At all the three scale levels, different types of theories and models are reviewed below.

1.2.1.1 Macroscopic Continuum Model

The macroscopic continuum theories model the hydrogel system as a continuous material composed of a network and fluid as well as charges. The theories concern the macroscopic characteristics of the hydrogel, instead of microscopic behavior. Usually

this type of theories characterizes the behavior of the hydrogel in the solution, and thus couples mass transport and deformation. Furthermore, they consider the effects of mechanical and chemical loads as well as electric fields.

Grimshaw *et al.* (1990) developed a model, which incorporates ionic transport, dissociation of fixed charge groups, simultaneous interstitial fluid flow, and mechanical deformation of the gel matrix, by coupling chemistry and mechanics together through a chemically-dependent swelling stress. Segalman *et al.* (1992) presented a model for the electromechanical gels incorporating kinematics of large deformation for two-dimensional finite-element computation (Segalman *et al.*, 1993). Chu *et al.* (1995) combined both kinetics and thermodynamics to predict the swelling process of polyelectrolyte gels with consideration to the influence of the buffer solution, mechanical relaxation and hydration degree of the gel. Gennes (2000) proposed an electromechanical formulation for ionic gels. Wallmersperger *et al.* (2008; 2001a; 2004; 2001b; 2007) presented a chemo-electro-mechanics coupled multi-field formulation to give more precise insight into the phenomena occurring in polyelectrolyte gels, where the ionic concentrations and the electric field are calculated by chemical and electrical equations, and the deformation behavior of the hydrogel is governed by the mechanical equilibrium equation. Based on the fundamental work of Grimshaw *et al.* (1989), De *et al.* (2002) improved a model for the simulation of equilibrium and kinetics of swelling pH-sensitive hydrogels, by incorporating the electro-static effect and fluid velocity (De and Aluru, 2004). Dolbow *et al.* (2004, 2005) presented a continuum model for chemically induced volume transition of the hydrogel, which allows for a sharp interface separating the swelled and collapsed phases of the underlying polymer network. Li's group developed three multiphysics models for the simulation of pH-sensitive hydrogels by the MECpH model, temperature-sensitive hydrogels by the MECtherm model, and electric-sensitive hydrogels by the MECe model, respectively (Li, 2009).

Recently Suo's group has worked actively in this area. They proposed a continuum theory for elastomer that responds to electric fields (Zhao *et al.*, 2007, 2008; Zhao and Suo, 2007). This theory is able to analyze the instability of the dielectrics under high electric potential (Zhao and Suo, 2007). They also proposed a nonlinear field theory coupled with diffusion and large deformation in polymeric gel, based on the nonequilibrium thermodynamics and kinetics (Hong *et al.*, 2008), which is applied successfully to analyze the behavior of gels in a solvent by finite element method

(Hong *et al.*, 2009; Liu *et al.*, 2010; Zhang *et al.*, 2009). Furthermore, this group developed a theory for the constrained swelling of pH-sensitive hydrogel (Marcombe *et al.*, 2010), and a theory for polyelectrolyte gel in an ionic solution (Hong *et al.*, 2010).

The above continuum models consider the hydrogel as a single system, generally composed of several partial differential equations (PDEs) that govern different fields. Therefore, they are more or less a theoretical framework, which may be imposed with different constitutive models.

1.2.1.2 Mixture Theory

In the mixture theories, the hydrogel is considered as a type of porous media with two or three phases, namely the solid network, fluid and/or charge. Usually these theories are based on macroscopic continuum, and describe the different phases separately.

An early work may be the well-known poroelasticity theory as a typical biphasic theory (Biot, 1941), where the constitutive relation of the mixture of solid and fluid phases is formulated separately. One of the most important mixture theories is the biphasic theory proposed by Mow *et al.* (1980), where the three classical governing equations based on the conservations of the mass and momentum as well as energy are all applied to both the solid network and fluid. Based on this biphasic theory, a triphasic theory was developed further, where the three governing equations are applied to one more phase, i.e. the ionic species (Lai *et al.*, 1991). This triphasic theory combines the physico-chemical theory for ionic and polyionic solution with the biphasic theory mentioned above, in which governing equations are based on conservations of the mass and momentum for the different phases. By assuming unchanged mass densities of the solid, fluid and ionic phases, the continuity equation is given as

$$\frac{\partial}{\partial x_i} [\phi^s v_i^s + \phi^w v_i^w + \phi^+ v_i^+ + \phi^- v_i^-] = 0 \quad (1.1)$$

where ϕ^a and v^a are the volume fraction and velocity of the a th phase (s is for solid, w for fluid, $+$ and $-$ for cationic and anionic ions respectively). By neglecting body and inertial forces, the conservation of momentum leads to the governing equation for the solid phase as

$$\frac{\partial \sigma_{ij}}{\partial x_i} = 0 \quad (1.2)$$

The momentum equations for the fluid and ionic phases include the frictional forces between the phases, and they are thus expressed as

$$-\rho^w \frac{\partial \mu^w}{\partial x_i} + f_{ws} (v_i^s - v_i^w) + f_{w+} (v_i^+ - v_i^w) + f_{w-} (v_i^- - v_i^w) = 0 \quad (1.3)$$

$$-\rho^+ \frac{\partial \mu^+}{\partial x_i} + f_{+s} (v_i^s - v_i^+) + f_{+w} (v_i^w - v_i^+) + f_{+-} (v_i^- - v_i^+) = 0 \quad (1.4)$$

$$-\rho^- \frac{\partial \mu^-}{\partial x_i} + f_{-s} (v_i^s - v_i^-) + f_{-w} (v_i^w - v_i^-) + f_{-+} (v_i^+ - v_i^-) = 0 \quad (1.5)$$

where ρ^a and μ^a are the density and chemical potential of the a th phase. f_{ab} is the frictional coefficients between the a th and b th phases and assumed to be symmetric, i.e., $f_{ab} = f_{ba}$. The electroneutrality condition inside the hydrogel is imposed by

$$\sum_k z^k c^k + z^f c^f = 0 \quad (1.6)$$

where z^k and z^f are the valences of the mobile ion and fixed charge, c^k and c^f are the concentrations of the mobile ion and fixed charge. For an isotropic hydrogel with infinitesimal deformation, the constitutive equations are given as

$$\sigma_{ij} = -p \delta_{ij} - T_c \delta_{ij} + \lambda \text{tr}(\mathbf{E}) \delta_{ij} + 2l E_{ij} \quad (1.7)$$

$$\mu^w = \mu_0^w + \frac{1}{\rho_T^w} \left[p - RT \phi (c^+ + c^-) + B_w \text{tr}(\mathbf{E}) \right] \quad (1.8)$$

$$\mu^i = \mu_0^i + \frac{RT}{M_i} \ln [\gamma_i c^i] + z^i \frac{F \psi}{M_i} \quad (1.9)$$

$$c^f = c_0^f \left(1 - \frac{1}{\phi_0^w} \text{tr}(\mathbf{E}) \right) \quad (1.10)$$

where p is the pressure of the fluid phase, T_c is the chemical-expansion stress. λ and l are the Lamé constants. ρ_T^w is the true mass density of the water, and E_{ij} the strain tensor. ϕ is the osmosis coefficient and B_w a material constant. M_i and γ_i are the molecular weight and the activity coefficient of the i th ionic species. c_0^f

and ϕ_0^w are the initial fixed charge density and water fraction, respectively. The triphasic theory has been applied to analyze confined compressive swelling.

Based on the above triphasic model, Hon *et al.* (1999) proposed a set of formulations derived from the generalized first law of thermodynamics, in which the ionic concentration is expressed by the chemical energy, and the chemical-expansion stress by the electrostatic energy. Bowen (1980, 1982) demonstrated another biphasic theory by thermodynamics, where the stress tensor of the mixture is determined by the chemical potentials of both the phases. Huyghe and Janssen (1999; 1997) presented a set of balance laws for solid, fluid, anions and cations, to formulate the quadriphasic theory, in which the effects of chemical, electrical, mechanical and/or thermal fields are considered. Zhu *et al.* (2010) developed a thermomechanical theory for multiphase transport in swelling unsaturated porous media on the basis of the mixture theory.

The mixture theory may describe the behavior of the hydrogel more completely. However, it is difficult to characterize the interaction between different phases.

1.2.1.3 Kinetic Theory

The kinetic theory concentrates mainly on the description of the equilibrium process of the hydrogel, including the swelling/shrinking process with time evolution.

The earliest work may be attributed to Biot (1941; 1955, 1956) for the analysis of poroelasticity, where Darcy's law governing the fluid flow in porous media is combined with linear elasticity. The fluid pressure contributes to the stress of the porous media in addition to mechanical elastic strain. The deformation is dependent on the fluid flow and evolves with time. Biot's theory is composed of the four governing equations in three-dimensional domain as follows

$$\frac{\partial^2 u_I}{\partial x_J \partial x_J} + \frac{1}{1-2\nu} \frac{\partial \varepsilon}{\partial x_I} - \frac{\alpha}{G} \frac{\partial p}{\partial x_I} = 0 \quad (1.11)$$

$$\frac{\alpha}{k} \frac{\partial \varepsilon}{\partial t} + \frac{1}{kQ} \frac{\partial p}{\partial t} = \frac{\partial^2 p}{\partial x_J \partial x_J} \quad (1.12)$$

where u_I is displacement in the I th direction, and p is the fluid pressure. G and ν are the well-known shear modulus and Poisson's ratio in classical elasticity theory. k is the coefficient of permeability in Darcy's law. α and Q are two coefficients depending on the degree of saturation of the porous media. ε is the first

invariant of the strain tensor and is a function of water pressure. In 3-D, the theory governs the field variables u_I and p . Biot's theory was developed by considering the kinetics of mass transport, instead of the dynamics of mechanical field, and it can work well for porous materials. Following Biot's idea, other kinetic theories were also presented by coupling mass transport and deformation with various concepts for different hydrogels (Birgersson *et al.*, 2008; Grimshaw *et al.*, 1990; Hong *et al.*, 2008; Ji *et al.*, 2006).

Tanaka and Fillmore (1979) presented a simple kinetic theory for swelling of gels, where friction between the polymer and liquid is considered. The theory is expressed in polar coordinate system as

$$\frac{\partial u}{\partial t} = D \frac{\partial}{\partial r} \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u) \right] \quad (1.13)$$

where u is the radial displacement, and r is the radius. D is diffusion coefficient of the gel and given by

$$D = \frac{K + 4G / 3}{f} \quad (1.14)$$

where K and G are the bulk and shear moduli, respectively, f is the friction coefficient between the polymeric network and fluid. This theory is based on Hook's law, and it is not accurate if the swelling ratio is very large.

In order to predict mass variation during the swelling of the hydrogel, Ritger and Peppas (1987) introduced a simple exponential relation,

$$\frac{M_t}{M_\infty} = kt^n \quad (1.15)$$

where M_t is the mass of the hydrogel at time t , M_∞ is the mass at equilibrium state. k is a characteristic constant of the hydrogel, and n is the diffusion exponent of the mode of mass transport. This relation is usually employed to fit experimental data and analyze the solvent transport mechanism of the hydrogel (Caykara and Dogmus, 2005; Wu *et al.*, 2006; Yarimkaya and Basan, 2007).

1.2.1.4 Constitutive Model

A constitutive model is required to represent the relation between pairs of energy conjugate variables using minimal number of parameters, such as stress and strain,

chemical potential and molecular concentration, electric field and displacement. The constitutive relation can be constructed by nonequilibrium thermodynamics, where the free energy is expressed as a functional or function of the stress (strain), the chemical potential (concentration), the temperature as well as the electric field (electric displacement) (Schapery, 2000). In general, constitutive models of rubber elasticity, poroelasticity, viscoelasticity and/or viscoplasticity are popular for modeling of hydrogels.

Usually the free energy for rubber elasticity is developed on the basis of the statistical mechanics. The Neo-Hookean model (Treloar, 1975) is a classical constitutive model for rubber elasticity, in which the function of strain energy density is given by

$$W = G(I_1 - 3) / 2 \quad (1.16)$$

where G is the shear modulus, I_1 is the first invariant of the left Cauchy-Green deformation tensor. The Neo-Hookean model was also extended in various forms for compressible and incompressible materials (Ogden, 1998). In brief, the Neo-Hookean models are simple in form and easy for implementation. However, they do not account for the dissipative release of energy, and assume perfect elasticity at all the stages of the deformation. Based on the Neo-Hookean theory, the Mooney-Rivlin model was developed for incompressible materials (Treloar, 1975), where the function of free energy density is defined as

$$W = C_1(\bar{I}_1 - 3) + C_2(\bar{I}_2 - 3) \quad (1.17)$$

where C_1 and C_2 are material parameters, $\bar{I}_1$ and $\bar{I}_2$ are the first and second invariants of the deviatoric component of the left Cauchy-Green deformation tensor. Apart from the Neo-Hookean theory and its extensions, other rubber elastic models were also developed. For instance, Flory and Erman (1982) constructed a constrained junction model, in which the contribution of intermolecular effect to the phantom network is described in the free energy. Drozdov (2007) improved the Flory-Erman model by expressing the free energy in terms of the two invariants of the Cauchy-Green tensor. Arruda and Boyce (1993b) proposed a model with a series expression, where the free energy is assumed as the sum of the strain energy of the individual chains oriented randomly in space. It can recover the Neo-Hookean theory if the number of rigid molecular segments in a polymer chain is large enough. Other contributions can also be found (Drozdov and Gottlieb, 2005; Erman, 2010; Hansen *et*

al., 2008; James and Guth, 1953). All the constitutive models mentioned above are based on the assumption that the gel/rubber behaves hyperelastically. They only consider the characteristics of the solid phase of the gel/rubber.

The understanding of nonlinear viscoelastic-plastic behavior of hydrogel still remains poor, although existing constitutive theories can handle the characteristics with varying degree of success (Anand and Ames, 2006). One of the most substantial works in this area is a 1-D rheological model proposed by Haward and Thackray (1968), where elastic intermolecular interaction, rate-dependent macro-yielding, and strain hardening are modeled by a combination of linear and nonlinear springs as well as viscous dashpots in a 1-D domain. This was then extended to 3-D (Anand and Ames, 2006; Arruda and Boyce, 1993a; Boyce *et al.*, 1988). Schapery (1997) proposed an approach for the modeling of mechanical behavior of fiber plastics, where intrinsic nonlinear viscoelastic and viscoplastic behaviors are taken into account. Chen and Schweizer (2008) built a constitutive equation based on the well-known generalized Maxwell model for the nonlinear mechanical response of polymer glass, where the deformation-dependent elastic modulus and alpha relaxation time are considered. Hasanpour and Ziaei-Rad (2008) presented a 3-D viscoelastic-plastic model for polymers, in which the stress is decomposed into viscoelastic and elastic-plastic components for finite element computation and comparison with experiments. Other viscoelastic-plastic constitutive models were also presented (Malkin, 2009; Schapery, 2000; Wineman, 2009).

Poroelasticity accounts for the performance of the two phases of the hydrogel, namely, the solid network and the fluid. Biot's formulation may be the first work in this area for the 3-D isotropic poroelasticity (Biot, 1941),

$$\varepsilon_{IJ} = \frac{\sigma_{IJ}}{2G} - \left(\frac{1}{6G} - \frac{1}{9K} \right) \delta_{IJ} \sigma_{KK} + \frac{1}{3H} \delta_{IJ} p \quad (1.18)$$

$$\varsigma = \frac{\sigma_{KK}}{3H_1} + \frac{p}{R} \quad (1.19)$$

where σ_{IJ} is the stress, p the fluid pressure, ε_{IJ} the strain, ς the variation in fluid content. G , K , H , H_1 , and R are material parameters. δ_{IJ} is the Kronecker delta notation. In Biot's theory, the fluid pressure contributes to the stress of the solid network, and the stress also influences the fluid content in the hydrogel. Biot also extended this isotropic model to an anisotropic one (Biot, 1955). Poroelasticity is a

popular constitutive relation for modeling of hydrogels in the mixture theory (Bowen, 1980; Hon *et al.*, 1999; Kluge *et al.*, 2010).

Apart from the constitutive models mentioned above, other constitutive relations were also developed for modeling of polymers by various concepts (Bhave *et al.*, 1993; Likhtman and Graham, 2003; Malkin, 2009).

1.2.1.5 Flory-Huggins Theory

Perhaps, Fowler and Rushbrooke made the first attempt to extend the statistical theory for pure solution to a liquid mixture, in which the molecules are distinctly unequal in size (Fowler and Rushbrooke, 1937). Huggins (1941) proposed a quantitative theoretical treatment to extend the theory developed by Fowler and Rushbrooke. Considering the limitation of the treatment for dilute polymer solutions proposed by Huggins, Flory (1941) developed a generalized statistical treatment applicable to high polymer solutions at all levels of concentrations on the basis of Meyer's model (Meyer, 1940). The framework proposed by Flory and Huggins is commonly known as the Flory-Huggins theory. This thermodynamic theory describes the change in free energy due to the mixing of the solvent molecules and polymeric chains. The mixing energy comes from the entropy and the enthalpy of mixing, given as

$$W_{mix} = RT \left[C \ln \frac{vC}{1 + vC} - \frac{\chi}{1 + vC} \right] \quad (1.20)$$

where R and T are the gas constant and temperature, respectively. v and C are the volume and concentration of the solvent molecules. In the model, the specific dimensionless parameter χ is the only material constant and it indicates the polymer-solvent interaction. If $\chi < 0$, the enthalpy of mixing motivates the solvent molecules to enter into the polymer network. When $\chi > 0$, the enthalpy of mixing motivates the solvent molecules to leave the polymer network (Hong *et al.*, 2008). This theory is based on the assumption that each solvent molecule or polymeric chain segment occupies one site exactly on a lattice, and all the polymeric chains have the same size.

The Flory-Huggins theory illustrates the mixing energy between the polymer and the solvent only, but it does not provide the expansion of the polymeric chains. Therefore, it is usually combined with energy contributed from elastic deformation of

the polymer to predict the characteristics of the hydrogel (Calderer *et al.*, 2010; Dusek and Patterson, 1968).

1.2.1.6 Flory-Rehner Theory and the Extension

Apart from the mixing energy between the polymeric chain and solvent mentioned in Subsection 1.2.1.5, there is another free energy change due to the stretching of the solid network of polymers. Flory and Rehner (1943a) proposed the entropy change due to the deformation of the polymeric network, based on statistical mechanics and rubber elasticity, in which the polymer chains are assumed to interact each other and the end-to-end distances of the polymer chains exhibit a Gaussian distribution. The free energy change due to the rearrangement of the polymer chains is presented as (Flory and Rehner, 1943a)

$$W_{str} = \frac{1}{2} NkT (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 2 \ln \lambda_1 \lambda_2 \lambda_3 - 3) \quad (1.21)$$

where N is the number of polymer chains per unit volume of the dry hydrogel, kT is the temperature in the unit of energy, and λ is the stretching ratio in different directions.

Based on the Flory-Huggins and above theories, Flory and Rehner (1943b) concluded that the swelling of crosslinked polymeric network results from the change in free energy due to mixing and stretching (Flory, 1953),

$$\begin{aligned} W &= W_{mix} + W_{str} \\ &= RT \left[C \ln \frac{vC}{1+vC} - \frac{\chi}{1+vC} \right] + \frac{1}{2} NkT (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 2 \ln \lambda_1 \lambda_2 \lambda_3 - 3) \end{aligned} \quad (1.22)$$

where W is the total free energy change during the swelling of the polymer.

This conclusion is widely known as the Flory-Rehner theory, and it is used commonly to explain or fit experimental results (Baker *et al.*, 1995; Unal and Hedden, 2009). The Flory-Rehner theory is a material model to characterize how the free energy of a gel system including the polymeric chain and the solvent changes during the swelling or shrinking of the gel. It provides the energy form for the general gel system. It is simple enough and only includes the two material-specific parameters, the polymer-solvent interaction χ and number of polymer chains N .

In order to apply the Flory-Rehner model to various hydrogels, researchers have tried to extend it. By considering the effects of the ionic contribution, the ionization of

the fixed charge, and the equilibrium between the charged group and hydrogen ions to the total free energy, Branon-Peppas and Peppas (1991) extended the Flory-Rehner theory to predict the equilibrium swelling of pH-sensitive hydrogels. Following a similar idea, Okay *et al.* (1998) predicted the equilibrium swelling of a negatively charged hydrogel in salt solution with an extension of the Flory-Rehner model, and concluded that an extended theory could correctly predict the swelling behavior of hydrogels up to 80 mol % charge densities. In Okay's model however, no ionization of fixed charge is included, and there is no equilibrium reaction between the fixed charge group and mobile ions, since it is supposed to predict the swelling/shrinking of the hydrogel in high concentration salt solutions. Based on the Flory-Rehner theory, Michaeli and Katchalsky (1957) developed a model combining the dependence of the degree of ionization of loosely crosslinked and highly swollen gels with the pH of an external medium. Apart from the stretching and mixing free energy, Ricka and Tanaka (1984) added the entropy contribution into the free energy due to the dissociation of the fixed charges W_{dis} and the Coulombic interaction W_{Col} between the charges, i.e.,

$$W = W_{str} + W_{mix} + W_{dis} + W_{Col} \quad (1.23)$$

This theory was applied to weakly charged ionic gels. Other extensions of the Flory-Rehner theory can also be found (Anthony *et al.*, 1996; Hong and Bae, 2002; Rainer *et al.*, 2000).

1.2.1.7 Lattice Model

The lattice model is defined in a lattice, instead of a continuous space. Therefore, it is possible to place different types of molecules in the lattice, such as polymer and solvent molecules. The simplest and most popular lattice theory is the Ising model, in which the state of a node in the lattice is represented by a discrete variable -- the spin. Each spin interacts only with its nearest neighbor, namely the short range interaction (Brush, 1967). One of the main purposes of using the lattice model for theoretical development of hydrogels is to predict the energy change after the mixture of a solution with the hydrogel.

Based on the Ising model, a lattice-cluster theory (LCT) was developed, termed Freed's theory, which is formally an exact mathematical solution of Flory-Huggins theory for interacting and self-avoiding polymers (Freed, 1985; Pesci and Freed, 1989). After that, a double-lattice model was introduced based on Freed's theory, in which

ordinary polymer solutions are described by the primary lattice, and oriented interactions are accounted for by a secondary lattice (Hu *et al.*, 1991). Sanchez and Lacombe (1976) applied the Ising model to pure fluids and a mixture of fluid and polymer, and developed a lattice-fluid model. Marchetti *et al.* (1990) extended the lattice-fluid model through the addition of the elastic term to the Flory-Rehner theory, and proposed a molecular theory for swollen gel.

All the lattice models mentioned above can be treated more or less as extensions or improvements of the classic Flory-Huggins theory. Apart from these lattice models, other efforts were made (Huang *et al.*, 2008; Lele *et al.*, 1995; Ray *et al.*, 1998).

1.2.1.8 Donnan Equilibrium Theory

When the contribution of the ionic species in a solution is considered in the free energy of the system for the charged hydrogel, the Donnan equilibrium theory is widely applied. The existence of Donnan effect was found first over semi-permeable biological cells. When it is applied to hydrogel modeling, the hydrogel-solution interface is taken to be a semi-permeable membrane, over which an osmotic potential is formulated. The Donnan equilibrium condition is given in the form as (Malmivuo and Plonsey, 1995)

$$\left(\frac{c^+}{\bar{c}^+} \right)^{\frac{1}{z^+}} = \left(\frac{\bar{c}^-}{c^-} \right)^{\frac{1}{z^-}} = \beta \quad (1.24)$$

where c^+ and $\bar{c}^+$ are the concentrations of positive ions in the hydrogel and solution, respectively. c^- and $\bar{c}^-$ are the concentrations of negative ions in the hydrogel and solution, respectively. z^+ and z^- are the valences of positive and negative ions respectively. β is the Donnan partitioning ratio. The advantage of the Donnan equilibrium is that it can simply obtain the ionic concentration inside the hydrogel by taking the ionic concentrations outside the hydrogel as known values; although it is difficult to measure ionic concentrations experimentally (Ricka and Tanaka, 1984).

The applications of the Donnan law at least date back to Inagaki (1957), where osmotic equilibrium was considered by the Donnan method. Ricka and Tanaka (1984) analyzed the quantitative consistency of the Donnan theory on the swelling of ionic charged gels, and concluded that it is well consistent as long as no divalent ions are

involved. Okay and Sariisik (2000) combined the Flory-Rehner theory with the Donnan equilibrium theory to predict the volume swelling ratio, and compared the theory with experimental swelling data for poly(acrylamide-*co*-sodium acrylate) hydrogel swollen in water and in aqueous salt (NaCl) solution, respectively. Horkay *et al.* (2000) developed a model, in which the Donnan theory was employed to calculate the effect of the difference between mobile ionic concentrations on the inside and outside of the gel. Hooper *et al.* (1990) demonstrated a model based on the ideal Donnan theory to describe the effects of fixed charge density and ionic strength on swelling equilibrium of neutral and strongly charged ionized hydrogels. The above three theories are also the extensions of the Flory-Rehner theory. De *et al.* (2002) also used the Donnan theory to obtain the concentration of salt ions inside hydrogels, with known concentration of hydrogen ions in both the hydrogel and solution domains.

Most of the utilization of the Donnan law in modeling of hydrogel aims to predict the ionic concentration inside the hydrogel, by assuming that the concentrations of ions in the solution are constant. Although it is simple enough, there still are limitations, such as inaccuracy for high concentration solution and multivalent ions.

1.2.1.9 Molecular Dynamics

Molecular dynamics (MD) simulations, as a deterministic method, can predict the behavior of interacting particles, such as atoms, molecules, and granules, in a system with time evolution (Zeng *et al.*, 2008), where the interaction potentials between particles and the force field characterize the movement of the particles and other properties of the system. Therefore, the key to develop the MD model for hydrogel is how the interaction energy and/or force field are specified. Due to the microscopic view of MD simulations, it can be applied to investigate most properties of hydrogels and polymers, such as free energy change, stability, diffusion, mechanical stress, and electric behavior.

Cornell *et al.* (1995) proposed a two-body molecular mechanical force field for simulation of the structures, conformational energy and interaction energy of hydrogels in a condensed phase. The model was implemented to analyze the conformation of poly(allylamine hydrochloride) in electrolyte solutions with various pHs and ionic strengths, and compared with experiments (Jachimska *et al.*, 2010). Moreno *et al.* (2010) presented a molecular modeling study for several polymers,

where the crystal structure of the polymers was found to be stable and corresponded to a well-defined energetic minima. Dhondi (2009) studied the mixing of shear thinning polymeric fluid in a long channel with patterned boundaries with an oscillating body force and found that the transverse flow increased significantly. Vorselaars *et al.* (2009) investigated the mechanism of strain hardening in glassy polymers with molecular dynamic simulation, and concluded that the simulations supported the experimental results. Harder *et al.* (2009) proposed an equilibrium MD method for investigating the properties of an aromatic polyamide reverse osmosis membrane, where the simulation was conducted to determine the density and diffusivity of water within the membrane fair agreement with experimental data was achieved. Varshney *et al.* (2009) analyzed the heat transfer in a thermoset polymer using atomistic molecular dynamics simulations by the consistent valence force field. Zhou and Daivis (2009) presented a coarse-grained model for MD simulation of polymer solutions with variable solvent, in which all interactions are short ranged and repulsive, making the model quite computationally efficient, compared with those with long ranged interactions. This model also includes the solvent explicitly, such that the theta condition, under which the polymer-polymer interaction and polymer-solvent interaction are balanced and thus the polymeric crosslink in the solvent does not expand, can correspond to a genuine cancellation of the solvent mediated polymer-polymer interactions. Dirama *et al.* (2008) studied the stress-strain behavior of the polymeric networks by MD simulation with a coarse-grained model, and demonstrated that the model could capture the fundamental mechanical features, such as yield behavior, strain hardening and failure. Sheldon *et al.* (2006) employed two different versions of the discontinuous MD model for the analysis of the collapse of polymers, and compared the simulation result with the off-lattice Flory theory with a good agreement.

Other molecular dynamic simulation techniques with different potential energy models and strategies for various purposes were also used to investigate the properties of hydrogels (Jang *et al.*, 2007; Mann *et al.*, 2006; Nara *et al.*, 2005; Palleschi *et al.*, 2006).

1.2.1.10 Monte Carlo Simulation

Similar to molecular dynamics simulations, Monte Carlo (MC) technique also handles problems at the molecular level. The difference between the two techniques is

that the MC method is a stochastic method which uses random numbers to generate a sample population of the system. The MC simulation usually probes the configuration of the system by trial movements of the particles, and accepts or rejects the new configuration by identifying the energy change. In other words, if the energy change is less than zero, the new configuration is always accepted. Otherwise, it is accepted with a probability governed by Boltzmann statistics. For modeling and simulation of hydrogels, the MC method is widely used to determine the properties of the system, such as diffusion, structural, and the swelling and mechanical properties.

Sikorski and Adamczyk (2010) proposed a model by the MC method to determine the structure and the dynamical properties of the polymer chains in a porous media, and concluded that the mobility of the chains decreases strongly with the number of obstacles. Meng *et al.* (2009) developed a model system for polymer blend with electron-donating and -accepting compounds, and subjected the model to dynamic MC simulations. Nowicki *et al.* (2010) analyzed the translocation of a polymer chain in a narrow hole by static MC simulation, and calculated the generalized thermodynamic force which governs the translocation. Edgecombe and Linse (2008) employed the MC method for simulating swelling and mechanical properties of various interpenetrating polymer networks, and found the different properties for charged and uncharged polymers. Schulz *et al.* (2006) studied ionic diffusion in a polymer network with the MC method, and compared the results with the dynamic percolation approach. Klos and Pakula (2004) carried out MC simulations of neutral solutions of strongly charged polymeric chains and counterions at various temperatures and monomer concentrations, and showed that chain behavior is dominated by the entropy itself if the polymer in the environment with high temperature. Khan and Chan (2003a) investigated the force extension behavior of charged polymers by MC simulation of strain and stress ensembles. Other MC approaches can also be found (Fergg and J. Keil, 2001; Khan and Chan, 2003b; Milchev *et al.*, 1999; Schneider and Linse, 2003; Zifferer *et al.*, 2002).

1.2.1.11 Other Microscopic Theories

Apart from the models mentioned above, significant effort was also made in other aspects to explain the amazing properties of hydrogels. For instance, Boryu and Erukhimovich (1988) proposed a microscopic statistical theory of polyelectrolyte

solution with polyions of low charge density in the random phase approximation, by taking into account the Debye-Hucker screening effect (Mitsuhiro *et al.*, 1996). Another important theory is Manning's condensation hypothesis (Manning, 1978), in which the counterions are assumed to bind to the polymer for reducing the effective charge density in the polymer to a constant value (Wennerström *et al.*, 1979). Levin *et al.* (1998) extended the Debye-Huckel-Bjerrum theory for the fluid state of a charged colloidal suspension, where the counterions are found to condense onto the charged system forming clusters, composed of one fixed charge and a number of counterions. The diffusive double layer and Stern layer theories are also popular for explaining the interaction between the mobile ions and the charged surface (Bagotsky, 2005).

1.2.2. Overview of Ionic-Strength-Sensitive Hydrogel

Ionic-strength-sensitive hydrogel is one of many stimuli-responsive hydrogels, which posses swelling or shrinking behavior in response to variations in ionic strength of the surrounding solution.

Numerous studies are conducted experimentally to synthesize or investigate the ionic-strength -sensitive hydrogels. For instance, Ohmine and Tanaka (1982) observed ionized acrylamide gels undergo discrete phase transition in equilibrium volume upon varying the ionic strength of the solution, and explained this phenomenon by the Flory-Huggins model and Donnan theory. Liu *et al.* (1995) studied the effect of ionic strength on the swelling properties of sulfonate gels in water and in various aqueous solutions. Jeon *et al.* (1998) studied the swelling behavior of polyelectrolyte gels for the effect of ionic strength at different initial monomer concentrations. Dhara *et al.* (Dhara *et al.*, 1999) synthesized interpenetrating networks of polymers to study the effect of different component contents on the swelling behavior of hydrogels, which illustrated the usual dependence on pH and ionic strength of the swelling medium. Zhao and Moore (2001) introduced a method for the preparation of pH- and ionic-strength-sensitive hydrogels that exhibit fast response and swelling/shrinking to ionic strength of the environment. Belma *et al.* (2005) prepared a series of acrylamide and *N*-vinylimidazole, named poly(AAm-*co*-NVI), to study the influence of ionic strength on the swelling behavior of hydrogels. Caykara and Dogmus (2005) studied the swelling/shrinking behavior of poly(Acrylamide-*co*-itaconic acide) hydrogel in water and aqueous NaCl solutions, and concluded that the equilibrium swelling ratio

of hydrogel increases drastically with the ionic strength of the external solution. Caykara and Aycicek (2005) synthesized ionic poly[(*N,N*-diethylaminoethyl-methacrylate)-*co*-(*N*-vinyl-2-pyrrolidone)], and examined the responsive characteristics of the hydrogel to external stimuli including ionic strength. Abd El-Mohdy (2007) prepared a novel hydrogel by grafting crosslinked polyacrylamide (PAM) chains onto carboxymethylcellulose (CMC), and showed the swelling properties of the hydrogel are dependent on the ionic strength of the solution. Lin *et al.* (2007) investigated the effects of ionic strength on the tensile properties of the hydrogel. Liu *et al.* (2007) prepared the acrylamide/maleic acid copolymer and examined the swelling/shrinking of the hydrogel in response to ionic strength and pH.

In terms of theoretical modeling, Flory (1953) is probably the first to introduce the contribution of the ionic strength of the surrounding solution into the swelling of hydrogel. However, Flory's technique could not handle the situation well when the ionic strength is considered as a stimulus to the hydrogel. Literature search reveals that few studies focus on the model development for ionic-strength-sensitive hydrogels, most of them applied the existing models for explanation of the experimental results concerning the influence of the ionic strength on the deformation behavior of the hydrogel. For example, Hooper *et al.* (1990) demonstrated a model capable of swelling equilibrium of neutral and ionized polyacrylamide gels in water or aqueous salt solution, and used Donnan theory for analysis of the effect of the ionic strength and fixed charge density on the swelling equilibrium, based on the extension of framework proposed earlier (Prange *et al.*, 1989). Baker *et al.* (1995; 1994) presented a simple Flory-type swelling model with Donnan theory concerning the swelling equilibrium of the hydrogel for comparison between simulation and experimental results, where the polyampholyte with negative fixed charge was synthesized and measured for analysis of the swelling equilibrium of the ionic-strength-sensitive hydrogel as a function of ionic strength and fixed charge (Baker *et al.*, 1992). English *et al.* (1996) showed an extension of the Flory-Huggins theory with a quasi-lattice screened Coulombic term for analysis of swelling ratio of the ionized hydrogel responsive to ionic strength, and predicted a qualitative agreement with the experimental results. Okay *et al.* (1998) utilized the Flory-Rehner theory to calculate the swelling ratio of anionic hydrogels in salt solution with the ionic strength ranging from 10^{-5} to 1 M , and compared simulation with experimental results, where the theoretical model can predict

accurately the swelling behavior for the limited charge densities. Caykara *et al.* (2000) derived an equation based on the model developed by Brannon-Peppas and Peppas (1991b) to study the equilibrium swelling behavior of hydrogels responsive to ionic strength. Peppas *et al.* (2000) gave the expressions of swelling ratio related to the ionic strength for the anionic and cationic hydrogels. Caykara *et al.* (2003) presented an equation based on Flory-Huggins thermodynamics theory, the James-Guth (1943) phantom network theory, and the Donnan theory, for investigation of the volume swelling ratio of hydrogels responsive to ionic strength.

1.3. Motivation and Objective

In most hydrogel-based applications, such as drug delivery, fluid control, biosensor, and bioactuators, smart hydrogels is often required to be immersed in a solution with certain ionic strength. Therefore, the response of the hydrogel to the change of the ionic strength cannot be ignored, since the ionic strength of the solution may induce the hydrogel to swell or shrink expectedly or unexpectedly. Based on the above literature survey however, it is known that few efforts have focused on model development for smart hydrogels responsive to the ionic strength of the surrounding solution, although many theoretical attempts were made for other environmental stimuli. It is thus necessary to give attention to the effect of the ionic strength on the responsive characteristics of the hydrogel.

Therefore, one of the main objectives of this thesis is to mathematically develop a multiphysics model for the analysis of the volume transition of smart hydrogels and the distribution of electric potential and ionic concentration in response to the change in the ionic strength of the bath solution. This is termed the multi-effect-coupling ionic-strength-stimulus (MECis) model. The model considers the coupled effects of different fields, including the chemical, electrical and mechanical fields, where the field equations govern mass conservation, the electric field, and momentum conservations in both the hydrogel and solution domains. Associated with the field equations, three sets of the constitutive laws are proposed, including the constitutive flux, the fixed charge equation, and the mechanical material law, which specify how the smart hydrogel responds to the change of the ionic strength in the solution by considering the influence of the ionic strength on the flux, the equilibrium reaction between the fixed charges and mobile ions, and the charge-to-charge repulsive force.

After the MECis model is developed, the next objective is to employ the model to analyze the equilibrium characteristics of ionic-strength-sensitive hydrogels. The steady-state form of the MECis model is applied firstly to analyze the equilibrium swelling ratios of various hydrogels which are responsive to the ionic strength when immersed in a solution. The simulation results are compared with corresponding experimental works in order to validate the steady-state MECis model. Then the steady-state MECis model is also compared with the other theories, including the modified Flory-Rehner theory-I and -II, and the gel-swelling model. After that, the influences of several important physical and chemical parameters on the equilibrium characteristics of the ionic-strength-sensitive hydrogel are studied, in order to demonstrate the detailed chemical, electrical and mechanical behaviors of the hydrogel and surrounding solution, where the influence of these parameters on the swelling ratio, chemical, electrical, and mechanical fields is presented, and the distributions of several important field variables in both the hydrogel and solution are analyzed in details, such as the fixed charge density, the concentration of the mobile ion, the electric potential, and the polymeric network displacement.

The third objective is to investigate the kinetic characteristics of the ionic-strength-sensitive hydrogel by the transient MECis model, since most applications require the understanding of the kinetics of the hydrogel. The transient MECis model is employed to investigate the kinetics of the swelling/shrinking and/or reversible properties of various ionic-strength-sensitive hydrogels, and compared with corresponding experiments, in order to examine the transient MECis model. Furthermore, the influence of several chemical and physical parameters on the kinetic swelling/shrinking of the ionic-strength-sensitive hydrogel is studied systematically. The reversible kinetics, the influences of the initial fixed charge density and the Young's modulus on the kinetics of the ionic-strength-sensitive hydrogel are studied in details. The kinetics of swelling ratio with different parameters, the kinetic distributions of the significant field variables in both the hydrogel and solution, including the fixed charge density, the concentration of mobile ions, the electrical potential, and the polymer network displacement, are analyzed in details.

The fourth objective is to provide a finite element analysis for a gel in a solvent and the dielectrics under electromechanical load, since FEM is a classical and powerful tool for numerical analysis and has been recently extended for simulations of polymers. The finite element models are used to study several time-dependent or

time-independent characteristics of gel and dielectrics with various shapes and under different loads. The present finite element analysis provides a powerfully convenient way to analyze the behavior of gels and dielectrics in water and/or subject to electromechanical loads.

All the four objectives mentioned above are motivated by different aspects of interests and applications, and they are achieved successfully in this thesis.

1.4. Outline of Thesis

This thesis is composed of six chapters, and each of them consists of several subsections to make it systematic.

In Chapter 2, the 3-D theoretical framework of the multi-effect-coupling ionic-strength-stimulus (MECis) model is proposed, and then reduced to a 1-D model. The model is developed in the three different fields, namely the chemical, the electrical and the mechanical fields. These three field equations govern the mass, electric flux and momentum conservations of the hydrogel and solution. Associated with the three fields, three constitutive laws are developed to illustrate the material behavior of the hydrogel and solution, namely the constitutive flux, the fixed charge equation, and the material law.

In Chapter 3, the 1-D steady-state MECis model is applied to analyze the equilibrium swelling/shrinking of ionic-strength-sensitive hydrogels. Before that, numerical strategies for solving the steady-state model are presented, where the Hermite-cloud method is used to discretize the governing equations of the MECis model in the spatial domain. The MECis model is then solved to analyze the equilibrium swelling ratio of various ionic-strength-sensitive hydrogels, and the results are compared with the experiments. The model is also compared with other theories, such as the modified Flory-Rehner and Gel-Swelling theories. In order to explore the influence of chemical and physical conditions on the equilibrium swelling behavior of hydrogels, parametric studies are conducted in details, including the initial fixed charge density, Young's modulus, initial fixed charge distance, and equilibrium constant, respectively.

In Chapter 4, the kinetics of ionic-strength-sensitive hydrogels are simulated by the transient MECis model. The 1-D transient model is discretized by the Hermite-cloud method in the spatial domain, and by the implicit Newmark method in the temporal

domain. The model is then solved to investigate the kinetic swelling/shrinking ratio of different smart hydrogels, and compared with corresponding experimental works. The influences of various parameters on the kinetics of the ionic-strength-sensitive hydrogel are also studied in order to understand the swelling/shrinking characteristics of the hydrogel.

In Chapter 5, the deformation of the gel in a solvent is studied by the 3-D nonlinear finite element model, and the finite element formulation is developed for dielectrics under electromechanical load. For the gel in a solvent, the FE model is based on the field theory, and it is used to analyze the deformation patterns of the gel with various shapes in water, including wrinkling, folding, twisting, and waving. For dielectrics under electromechanical load, the FE formulation is developed on the basis of a nonlinear field theory for dielectrics. The behavior of dielectrics subject to an electromechanical load is investigated by the FE formulation. The formulation is also employed to analyze the behavior of dielectric gels in water and subjected to electromechanical load.

Finally, this thesis ends with important conclusions and proposed future work in Chapter 6, in which the present studies and contributions are summarized, and possible future works are recommended.

Fig. 1.1. The three-dimensional structure of the hydrogel, which is composed of the three phases, namely the 3-D network of crosslinked polymeric chains, the interstitial fluid, and the ionic species including the fixed charges and mobile ions.

2

Development of Multi-Effect-Coupling Ionic-Strength-Stimulus (MECis) Model

2.1. Introduction

The ionic strength is one of the most significant characteristics of electrolyte solutions, as it measures the concentration of mobile ions in the solution as stated in Chapter 1. It is important to understand how smart hydrogels respond to the ionic strength of a solution since the hydrogels are often immersed into solutions for applications such as microfluidic control, drug delivery, and BioMEMS.

In this chapter, a three-dimensional multiphysics model, termed the multi-effect-coupling ionic-strength-stimulus (MECis) model, is proposed for simulation of the chemical, electrical and mechanical behaviors of hydrogels responsive to the ionic strength of the surrounding solution. Subsequently, the model is reduced to a one-dimensional domain.

The MECis model is composed of three sets of nonlinear governing partial differential equations (PDEs) corresponding to three fields, namely the chemical, electric and mechanical fields. In addition, three sets of constitutive relations are also developed: the constitutive flux, the fixed charge equation, and the material law of the polymeric network. Totally the six sets of equations characterize the responsive behavior of mobile ions, the fixed charge, electric potential, and solid polymeric network. For the chemical field, the governing equation is based on the law of mass conservation of the ionic species within both the hydrogel and solution domains. The corresponding constitutive flux of mobile ions is driven by the gradients of the ionic strength, the ionic concentration and electric potential. For the electric field, the governing equation is based on the Gaussian law for distribution of electric potential in

both the hydrogel and bathing solution, in which the effect of the fixed charge is integrated. Based on the Langmuir isotherm theory for the interaction between the fixed charges and mobile ions, the fixed charge equation is developed for the effect of the ionic strength on the fixed charge density. For the mechanical field, the mechanical finite deformation governing equation is based on the law of momentum conservation, where the two driving forces, namely the osmotic pressure and repulsive force result from the chemical and electric fields. The osmotic pressure is due to the different concentrations of the interior hydrogel and exterior solution, while the repulsive force arises from the electrostatic force between the fixed charges.

In the MECis model, the ionic strength of the solution is explicitly incorporated into the constitutive relations from the chemical, electrical and mechanical aspects. It significantly influences the behavior of mobile ions, fixed charge, and polymeric network in both the hydrogel and solution domains. The MECis governing equations and constitutive laws are coupled together with capability of predicting the equilibrium and kinetic deformation of ionic-strength-sensitive hydrogels, as well as the characteristics of solution concentration and electric potential.

2.2. MECis Model in Three-Dimensional Domain

In fact, many experimental observations demonstrate that the responsive properties of hydrogels to the ionic strength may be induced by three contributions, including the chemical and electrical as well as mechanical effects. The chemical variation in the solution may induce the flux of mobile ions from gel to solution or vice versa, where the fixed charges bound in the hydrogel form an electric field around the hydrogel. The electric field may influence the fluxes of mobile ions, thus the fixed charges may also react with the mobile ions chemically or physically. The mechanical deformation of the polymeric network could be induced by the ionic concentration difference and electric field. The interacting effects of the chemical, electrical and mechanical fields are integrated into the present MECis model.

2.2.1. Configurations and Kinematics

Before the development of the MECis model, the reference configuration is defined by Lagrangian coordinate $\mathbf{X}$. In general, the reference configuration could correspond to the state of a hydrogel at any time. In the present work however, the

reference configuration refers to the state of the water-saturated hydrogel or an equilibrium state of the hydrogel immersed in a solution with an ionic strength, since the model focuses on the system response to the change of ionic strength.

At the reference state, a control volume around the particle $\mathbf{X}$ within the gel or solution is denoted by $dV(\mathbf{X})$, and the surface of the volume by $N_k(\mathbf{X})dS(\mathbf{X})$, where $dS(\mathbf{X})$ is the area of the surface and $N_k(\mathbf{X})$ is the unit vector normal to the surface. In a current state at time t after swelling or shrinking, the particle $\mathbf{X}$ occupies a place with Eulerian coordinate $\mathbf{x}(\mathbf{X}, t)$, as shown in Fig. 2.1. The deformation gradient $\mathbf{F}(\mathbf{X}, t)$ is therefore defined as

$$F_{iK} = \frac{\partial x_i(\mathbf{X}, t)}{\partial X_K} \quad (2.1)$$

The determinant of the deformation gradient is denoted by $\det(\mathbf{F})$, representing the change of the control volume around the particle $\mathbf{X}$ after deformation.

It is noted that nominal quantities defined in the reference configuration in Lagrangian coordinates are used dominantly in the present MECis equations. However, a few Eulerian forms of the equations and quantities are also employed to derive the formulation. In addition, the indicial forms of tensor and vector are used in the formulation of the MECis model, where the repeat subscript index is dummy, and implies the addition over it (see Appendix A). However, the repeat superscript of the ionic species does not represent a summation over it.

2.2.2. Chemical Field

The chemical field describes the characteristics of the ionic species, based on the law of mass conservation. Let $C^a(\mathbf{X}, t)$ be the nominal concentration of the a th ionic species, namely, $C^a(\mathbf{X}, t)dV(\mathbf{X})$ is the number of the a th ionic species in the control volume, which is related to the true concentration $c^a(\mathbf{X}, t)$ by

$$c^a(\mathbf{X}, t) = \frac{C^a(\mathbf{X}, t)}{\det(\mathbf{F})} \quad (2.2)$$

The mass conservation of mobile ions in the reference configuration leads to

$$\frac{D}{Dt} \int_V C^a(\mathbf{X}, t) dV = - \int_S J_K^a N_K dS + \int_V r^a dV \quad a = 1, 2, \dots \quad (2.3)$$

where D / Dt is the material derivative, $J_K^a(\mathbf{X}, t)$ is the nominal constitutive flux of the a th ionic species which constitutes the mass conservation equation, and $G^a(\mathbf{X}, t)$ is the generative or consumptive rate of the a th ionic species.

The material derivative in the reference configuration can be expressed in another form as

$$\frac{D}{Dt} \int_V C^a(\mathbf{X}, t) dV = \int_V \frac{\partial C^a(\mathbf{X}, t)}{\partial t} dV \quad (2.4)$$

The flux across the control surface could be converted by the well-known divergence theorem as

$$\int_S J_K^a N_K dS = \int_V \frac{\partial J_K^a}{\partial X_K} dV \quad (2.5)$$

The combination of Eqs. (2.3) to (2.5) results in

$$\int_V \left(\frac{\partial C^a(\mathbf{X}, t)}{\partial t} + \frac{\partial J_K^a(\mathbf{X}, t)}{\partial X_K} - r^a(\mathbf{X}, t) \right) dV = 0 \quad (2.6)$$

Since the control volume is taken arbitrarily, the integrand vanishes, such that Eqn. (2.6) can be rewritten in the differential form as

$$\frac{\partial C^a(\mathbf{X}, t)}{\partial t} + \frac{\partial J_K^a(\mathbf{X}, t)}{\partial X_K} = r^a(\mathbf{X}, t) \quad a = 1, 2, \dots \quad (2.7)$$

The above chemical field equation (2.7) governs the concentrations of the ionic species in both the hydrogel and solution domains. In order to specify the influence of ionic strength on the chemical field, the constitutive flux $J_K^a(\mathbf{X}, t)$ has to be determined.

2.2.3. Constitutive Flux

The flux in the chemical field equation (2.7) may be driven chemically and electrically. By Nanson's relation, the nominal constitutive flux $J_K^a(\mathbf{X}, t)$ is related to the true flux $j_K^a(\mathbf{x}, t)$ by

$$j_i^a = \frac{F_{iK}}{\det(\mathbf{F})} J_K^a \quad (2.8)$$

The true diffusion flux driven by the chemical potential can be expressed by the well-known Fickian law as

$$j_{I(d)}^a = - \frac{c^a(\mathbf{X}, t) D^a(\mathbf{X}, t)}{RT} \frac{\partial \mu^a(\mathbf{X}, t)}{\partial x_I} \quad (2.9)$$

where $\mu^a(\mathbf{X}, t)$ and $D^a(\mathbf{X}, t)$ are the chemical potential and diffusion coefficient of the a th ionic species. R and T are the gas constant and temperature, respectively. It is noted that the present diffusion coefficient $D^a(\mathbf{X}, t)$ is assumed to be isotropic for hydrogel and solution, respectively, it becomes a scalar. In fact, these true quantities are the updated Lagrangian description associated with markers in the reference configuration. The chemical potential $\mu^a(\mathbf{X}, t)$ may be expressed as (Alberty and Silbey, 1997)

$$\mu^a = \mu_0^a + RT \ln(c^a \gamma^a) \quad (2.10)$$

where μ_0^a is the chemical potential of the a th ionic species in an ideal solution, and γ^a is the chemical activity coefficient of the a th ionic species.

Taking the derivative of chemical potential with respect to Lagrangian coordinates leads to

$$\begin{aligned} \frac{\partial \mu^a(X, t)}{\partial X_K} &= \frac{RT \partial \ln(\gamma^a c^a)}{\partial X_K} = \frac{RT \partial \ln(\gamma^a)}{\partial X_K} + \frac{RT}{c^a} \frac{\partial c^a}{\partial X_K} \\ &= \frac{RT \partial \ln(\gamma^a)}{\partial X_K} + \frac{RT}{C^a} \frac{\partial C^a}{\partial X_K} \end{aligned} \quad (2.11)$$

By following the chain rule of partial derivative,

$$\frac{\partial \mu^a}{\partial X_K} = \frac{\partial \mu^a}{\partial x_i} F_{iK} \quad (2.12)$$

Combining Eqs. (2.8) to (2.12), the nominal diffusion flux $J_{K(d)}^a$ is given as

$$J_{K(d)}^a = -M_{KL}^a \left(\frac{1}{C^a} \frac{\partial C^a}{\partial X_L} + \frac{\partial \ln \gamma^a}{\partial X_L} \right) \quad (2.13)$$

where $M_{KL}^a(\mathbf{F}, C^a)$ is the mobility tensor of the a th ionic species, and defined as

$$M_{KL}^a(\mathbf{F}, C^a) = D^a C^a H_{iK} H_{iL} \quad (2.14)$$

where H_{iK} is the transpose of the inversion of the deformation gradient, namely, $H_{iK}F_{iL} = \delta_{KL}$ and $H_{iK}F_{jK} = \delta_{ij}$.

The activity coefficient γ^a accounts for the ion-ion interaction in the interstitial fluid of hydrogels, and is described by the extended Debye-Huckel law (Atkins and Paula, 2007)

$$\ln \gamma^a = \frac{-\alpha_1 z_a^2 \sqrt{\tilde{I}}}{1 + \alpha_2 \sqrt{\tilde{I}}} + \alpha_3 \tilde{I} \quad (2.15)$$

where α_1 , α_2 and α_3 are constants associated with the environmental conditions and deformation gradient. $\tilde{I}$ is the nominal ionic strength defined as

$$\tilde{I} = \frac{1}{2} \sum_m z_m C^m \quad (2.16)$$

The nominal ionic strength is related to the true ionic strength as

$$\tilde{I} = I \det(\mathbf{F}) \quad (2.17)$$

where the true ionic strength I is defined as (Sinko, 2006)

$$I = \frac{1}{2} \sum_m z_m c^m \quad (2.18)$$

Substituting Eqn. (2.15) into (2.13), the nominal diffusion flux is rewritten as

$$J_{K(d)}^a = -M_{KL}^a(\mathbf{F}, C^a) \left(\beta^a(\tilde{I}) \frac{\partial \tilde{I}}{\partial X_L} + \frac{\partial C^a}{C^a \partial X_L} \right) \quad (2.19)$$

where

$$\beta^a(\tilde{I}) = \left(\frac{-\alpha_1 z_a^2}{\sqrt{\tilde{I}} (1 + \alpha_2 \sqrt{\tilde{I}})^2} + \alpha_3 \right) \quad (2.20)$$

The true migration flux due to the existence of the electric force between the mobile ions in the hydrogel and solution is given by

$$j_{I(m)}^a = z_a \eta^a c^a E_I^f = \frac{z_a D^a F c^a}{RT} E_I^f \quad (2.21)$$

where $\eta^a = D^a F / (RT)$ is the electric mobility, F is the Faraday constant, and

E_I^f is the true electric field defined as the gradient of the electric potential $\psi(\mathbf{X}, t)$ in the Eulerian coordinate $\mathbf{x}$

$$E_I^f = -\frac{\partial \psi}{\partial x_I} \quad (2.22)$$

Similarly, the nominal electric field is defined as

$$\tilde{E}_I^f = -\frac{\partial \psi}{\partial X_I} \quad (2.23)$$

By the chain rule, the nominal electric field $\tilde{E}_I^f$ is related to the true electric field E_I^f by

$$\tilde{E}_I^f(\mathbf{X}, t) = F_{IJ} E_J^f(\mathbf{x}, t) \quad (2.24)$$

Therefore, the nominal migration flux $J_{K(m)}^a$ can be written as

$$J_{K(m)}^a = -M_{KL}^a \frac{z_a F}{RT} \frac{\partial \psi}{\partial X_L} \quad (2.25)$$

In conclusion, the constitutive flux J_K^a due to diffusion and migration is expressed as

$$J_K^a = -M_{KL}^a \left(\beta^a(\tilde{I}) \frac{\partial \tilde{I}}{\partial X_L} + \frac{\partial C^a}{\partial X_L} + \frac{z_a F}{RT} \frac{\partial \psi}{\partial X_L} \right) \quad a = 1, 2 \dots \quad (2.26)$$

Therefore, it is demonstrated from Eqn. (2.26) that the constitutive flux results from three sources, the respective gradients of ionic strength, concentration and electric potential. The above flux J_K^a is also generally known as the Nernst-Planck flux in Eulerian description.

2.2.4. Electric Field

The electric field characterizes the charges in the hydrogel and solution domains. As is well known, the spatial charges can be described in several ways, such as the constant field where the electric potential across the system varies linearly, the constant current where the electroneutrality occurs and the field equation where the electric potential is governed by a partial differential equation such as the well-known Poisson equation (De and Aluru, 2004; Wallmersperger and Kroplin, 2007) or nonlinear Poisson-Boltzmann equation (Carvalho *et al.*, 1998; Kagata *et al.*, 2001; Phillips, 2009). However, the Poisson-Boltzmann equation inherently assumes the equilibrium distribution of ions in the electric double layer, thus neglecting the

dynamic behavior of ions (Park and Choi, 2009).

In the present model, the field equation is developed for spatial charges. The charge density $Q(\mathbf{X}, t)$ in the hydrogel is composed of two sources: the fixed charge density C^f bound on the polymeric chains and the mobile charge density C^b in the interstitial fluid,

$$Q(\mathbf{X}, t) = F \left(z_f C^f(\mathbf{X}, t) + \sum_b z_b C^b(\mathbf{X}, t) \right) \quad (2.27)$$

where z_f is the valence of the fixed charge. However, the charge density in the solution is only composed of mobile ions. In order to make the formulation consistent, the above equation (2.27) is also applicable in the solution by letting $C^f = 0$.

Based on the Gaussian law, the nominal charge density $Q(\mathbf{X}, t)$ in the hydrogel and solution obeys

$$\int_S \tilde{D}_K(\mathbf{X}, t) N_K dS = \int_V Q(\mathbf{X}, t) dV \quad (2.28)$$

where $\tilde{D}_K(\mathbf{X}, t)$ is the nominal electric displacement. Based on Nanson's relation, it is related to the true electric displacement D_i by

$$D_i = \frac{F_{iK}}{\det(\mathbf{F})} \tilde{D}_K \quad (2.29)$$

By imposing the divergence theorem on the arbitrary control volume, Eqn. (2.28) is rewritten as

$$\frac{\partial \tilde{D}_K(\mathbf{X}, t)}{\partial X_K} = Q(\mathbf{X}, t) \quad (2.30)$$

The well-known relation between the true electric displacement field and true electric field is given as

$$D_i = \varepsilon E_i \quad (2.31)$$

where $\varepsilon(\mathbf{X}, t)$ is the permittivity of the system, and is purely the permittivity of the solution in the solution domain. In the hydrogel domain however, it depends on the permittivities of both the hydrogel and solution. For example, the permittivity of the hydrogel could be taken as the volumetric average of the solution and polymeric network

$$\varepsilon = \frac{V_n \varepsilon_n + V_s \varepsilon_s}{V_n + V_s} \approx \varepsilon_s \quad (2.32)$$

where ε_n and ε_s are the permittivities of the polymeric network and solution respectively, V_n and V_s are the volumes of the polymeric network and solution respectively. However, since the majority of the hydrogel is generally occupied by the solution, i.e. $V_s \gg V_n$, it is reasonable to impose the permittivity of the solution directly over the whole domain.

Combining Eqs. (2.23), (2.24), (2.29) and (2.31) together, the nominal electric displacement is expressed as

$$\tilde{D}_K(\mathbf{X}, t) = -\varepsilon \det(\mathbf{F}) H_{iK} H_{iL} \frac{\partial \psi(\mathbf{X}, t)}{\partial X_L} \quad (2.33)$$

The electric field in the hydrogel and solution is thus given as

$$\frac{\partial}{\partial X_K} \left[\varepsilon \det(\mathbf{F}) H_{iK} H_{iL} \frac{\partial \psi(\mathbf{X}, t)}{\partial X_L} \right] + F \left(z_f C^f(\mathbf{X}, t) + \sum_b z_b C^b(\mathbf{X}, t) \right) = 0 \quad (2.34)$$

The above Eqn. (2.34) characterizes the electric potential in both the hydrogel and solution domains in the reference state, and is named the Poisson equation in Eulerian form. It can be proven that the constant field and constant current are actually simplified cases of the present field equation. It is understood that the charge difference results in the existence of an electric field, which changes the distribution of mobile ions to achieve electroneutrality.

2.2.5. Fixed Charge Equation

The constitutive relation in the electric field is associated with the characteristics of the fixed charges. So far, the main research interest in this area is concerned with the interaction between fixed charges and mobile ions. One of the most important theories is Manning's condensation hypothesis (Manning, 1978), in which the counterions is characterized to bond to a charged rod in order to reduce the effective charge density of the rod (Wennerström *et al.*, 1979). This treatment can only be applied to the rod-shaped gel in an infinitely diluted solution. It is difficult to be applied in the modeling of high flexible hydrogels because of two important facts, namely, the ionic strength of the solution could be very high, and the hydrogel geometry is far from a rod (Schroder and Oppermann, 1996). In addition, Levin *et al.*

(1998) extended the Debye-Huckel-Bjerrum theory to the fluid state of a charged colloidal suspension. It was found that the counterions condense onto the charged system forming clusters composed of one fixed charge and a number of counterions. Furthermore, the diffusive double layer and Stern layer theories provide additional explanation of the interactions between fixed charges and counterions (Bagotsky, 2005). However, these theories only considered the interaction between fixed charges and mobile ions on the surface of the hydrogel but neglect the interaction inside the hydrogel.

Another important theory is the Langmuir adsorption isotherm theory, where the counterions are bound to the fixed charge sites via chemical reactions (De and Aluru, 2004; Grimshaw *et al.*, 1990; Nussbaum, 1986). In the present model, the Langmuir monolayer adsorption theory is modified to describe the interaction between mobile ions and fixed charges. The modification improves the present fixed charge equation by including the influence of the ionic strength of the solution.

Let us consider the interaction between fixed charges and mobile ions as

where M is the mobile ions, S the fixed charge sites of the hydrogel, MS the bound sites after the reaction, and K the dissociation constant. The above reaction (2.35) corresponds to the equilibrium between the dissociation and binding between fixed charges and mobile ions. The reaction (2.35) achieves an equilibrium state when the dissociation and binding processes are in balance.

If $C_{s,0}^f$ is the fixed charge density of the hydrogel at dry state, C_0^f the fixed charge density in the reference configuration, one has

$$C_0^f = C_{s,0}^f \phi_s^0 \quad (2.36)$$

where $\phi_s^0 = V_0^s / V_0$ is the volume fraction of the polymeric solid phase at the reference state of the hydrogel, and is defined as the volume ratio of the solid phase V_0^s to the total volume V_0 . Let us define C^b as the nominal concentration of the mobile ions bound to the fixed charge sites $[M]$, $C^f(\mathbf{X}, t)$ as the fixed charge density $[S]$, and $C_b^f = C_0^f - C^f$ as the density of the bound fixed charge sites $[MS]$. Based on the equilibrium reaction (2.35), the nominal dissociation constant $\tilde{K}$ is thus defined as

$$\tilde{K} = \frac{C^f C^b}{C_0^f - C^f} \quad (2.37)$$

The fixed charge density after bound reaction is therefore obtained as

$$C^f(\mathbf{X}, t) = \frac{\phi_0^s C_{s,0}^f \tilde{K}}{\tilde{K} + C^b} \quad (2.38)$$

Actually the Eulerian form of Eqn. (2.38) is the fixed charge model (De and Aluru, 2004; Grimshaw *et al.*, 1990; Luo *et al.*, 2008; Nussbaum, 1986), where the dissociation constant is not related to the ionic strength, based on the assumption that the hydrogel is immersed in a dilute solution. As is well known however, the ionic strength has substantial influence on the dissociation constant when the solution is non-ideal. Therefore, it is necessary to incorporate this important effect in the model.

The nominal dissociation constant is related to the true dissociation constant K by

$$\tilde{K} = \det(\mathbf{F})K \quad (2.39)$$

where the true apparent dissociation constant K is influenced by the ionic strength as (Sinko, 2006),

$$K = K_0 \exp \left[\frac{\alpha_1 \ln(10)(2|z_b| - 1)\sqrt{\tilde{I}}}{(1 + \alpha_2 \sqrt{\tilde{I}})} \right] \quad (2.40)$$

where K_0 is the true intrinsic dissociation constant and it is related to the nominal intrinsic dissociation constant by $\tilde{K}_0 = \det(\mathbf{F})K_0$. z_b is the charge number of the bound ions. The nominal fixed charge density at the current state C^f is thus given as

$$C^f(\mathbf{X}, t) = \frac{\phi_0^s C_{s,0}^f \tilde{K}_0 \exp \left[\alpha_4(z_b)\sqrt{\tilde{I}} / (1 + \alpha_2 \sqrt{\tilde{I}}) \right]}{\tilde{K}_0 \exp \left[\alpha_4(z_b)\sqrt{\tilde{I}} / (1 + \alpha_2 \sqrt{\tilde{I}}) \right] + C^b} \quad (2.41)$$

where

$$\alpha_4(z_b) = \alpha_1 \ln(10)(2|z_b| - 1) \quad (2.42)$$

The above constitutive fixed charge equation (2.41) illustrates the interaction between the fixed charges and mobile ions on the basis of the influence of ionic strength.

The binding of mobile ions to the polymeric chains depends on the complicated interaction between mobile ions in the interstitial fluid and fixed charge groups. Usually, all the counterions tend to be bound to the polymeric chains if the hydrogel is

immersed in the salt solution with multiple ionic species. However, these counterions are bound with different rates. For example, for the poly(sodium acrylate-co-hydroxyethyl methacrylate) (SA-co-HEMA), the tendency of binding rates follows $\text{LiCl} = \text{NaCl} = \text{KCl}$, $\text{CaCl}_2 < \text{SrCl}_2 < \text{BaCl}_2$, and $\text{Fe}^{3+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ (Lee and Wu, 1996); for the poly[sodium acrylate-co-*N,N*-dimethyl(acrylamidopropyl) ammonium propane sulfonate] (SA-co-DMAAPS), the tendency of binding rates follows $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+}$ (Lee and Yeh, 1997). The experiments also provide several tendencies of binding rates for other smart hydrogels (Horkay *et al.*, 2000; Kudo *et al.*, 1993; Pourjavadi *et al.*, 2006). In the present MECis model, if the hydrogel is immersed into a mixed salt solution with multiple ionic species, the species with the fastest rate of binding in the tendency is considered as the mobile ions C^b bound to the polymeric chains of the hydrogel.

2.2.6. Mechanical Field

The mechanical field demonstrates the deformation of the hydrogel concurrently with the effects of ionic transport and electric field. Based on the law of conservation of momentum, the mechanical equation can be expressed as

$$\frac{D}{Dt} \int_V \rho v_K dV = \int_S T_K dS + \int_V B_K dV \quad (2.43)$$

where ρ is the density of the hydrogel, v_K is the velocity field of the hydrogel, b_K is the body force vector, T_K is the traction field on the surface of the hydrogel.

By Cauchy's law, the nominal stress P_{iK} could be defined as

$$P_{iK} N_i = T_K \quad (2.44)$$

Using the divergence theorem, neglecting inertial term, and noting the arbitrariness of the control volume, Eqn. (2.43) is rewritten as

$$\frac{\partial P_{iK}(\mathbf{X}, t)}{\partial X_i} + B_K(\mathbf{X}, t) = 0 \quad (2.45)$$

Here, it is reasonable to neglect the inertial term since the swelling/shrinking of the hydrogel is quite slow (De and Aluru, 2004; Hong *et al.*, 2008), and the momentum is in equilibrium at all times. The above mechanical equation (2.45) describes the

deformation and stress fields in the hydrogel, where the stress is determined by the deformation and material properties.

2.2.7. Material Law

The deformation behavior of hydrogels follows the material law. In terms of the polymeric solid phase of hydrogels, two contributions to the free energy are considered in the present model, namely the elastic energy W_{ela} and electric energy W_{ele} ,

$$W = W_{ela} + W_{ele} \quad (2.46)$$

The free energy density due to the elastic strain is commonly known as

$$W_{ela}(\mathbf{F}) = \frac{1}{2} S_{iK} E_{iK} \quad \text{and} \quad S_{iK} = P_{iJ} H_{JK} \quad (2.47)$$

where S_{iK} is the second Piola-Kirchhoff stress, and E_{iK} is the Green strain. This is the linear elasticity with nonlinear geometry or large deformation.

The free energy density due to the electrostatic field of the fixed charges in the polymeric network can be expressed by

$$W_{ele}(\mathbf{F}, C^f) = \frac{1}{2} N_A q C^f \omega(\mathbf{F}) \quad (2.48)$$

where N_A is Avogadro's constant, $\omega(\mathbf{F})$ is the electrostatic potential of an elementary charge q and it could be written as

$$\omega(\mathbf{F}) = \frac{q}{4\pi\epsilon \det(\mathbf{F}) |\mathbf{R}|} \exp\left(-\frac{\det(\mathbf{F})^{1/3} |\mathbf{R}|}{\kappa}\right) \quad (2.49)$$

where $|\mathbf{R}|$ represents the distance between the two charges in the reference configuration, and κ is the Debye shielding radius and defined as

$$\kappa = \sqrt{\frac{\epsilon R T \det(\mathbf{F})}{2 F^2 \tilde{I}}} \quad (2.50)$$

Therefore, the nominal stress due to the elastic and electric energies is formulated as

$$\begin{aligned}
 P_{iK} &= \frac{\partial W}{\partial F_{iK}} \\
 &= S_{iJ} F_{KJ} - \frac{FC^f q}{24\pi\epsilon |\mathbf{R}|} \left(\frac{\kappa + \det(\mathbf{F})^{1/3} |\mathbf{R}|}{\det(\mathbf{F})^{1/3} \kappa} \right) \exp \left(- \frac{\det(\mathbf{F})^{1/3} |\mathbf{R}|}{\kappa} \right) H_{iK}
 \end{aligned} \quad (2.51)$$

The second term in the right-hand side of the above equation (2.51) results from the electric energy due to the charge-to-charge electrostatic repulsive force on the polymeric network of the hydrogel. The stress due to the electrostatic energy is also termed as the chemical-expansion stress (Lai *et al.*, 1991).

Since the hydrogel is a porous medium, both the stress of polymeric solid phase and the pressure of fluid exist. When hydrogel is immersed into a solution at equilibrium state, the pressure difference of the solvent between the interior hydrogel and the exterior solution can be neglected, if no solvent flow is assumed in the system. However, there exists osmotic pressure over the hydrogel-solution interface due to the difference of the ionic concentrations. The ionic contribution to the stress π^{ion} is generally written in the Eulerian form by (Flory, 1953; Hooper *et al.*, 1990)

$$\pi^{ion} = RT \sum_a (c^a - c_0^a) \quad (2.52)$$

where c^a and c_0^a are the ionic concentrations in the deformed configuration of the hydrogel and the solution, respectively. By Nanson's relation, it can be converted to the reference configuration with the Lagrangian coordinates, thus the nominal osmotic pressure Π_{iK}^{ion} is written as

$$\Pi_{iK}^{ion} = RT \sum_a (C^a - \det(\mathbf{F}) c_0^a) H_{iK} \quad (2.53)$$

Following Biot's theory (Biot, 1941), the total stress is expressed as

$$\begin{aligned}
 P_{iK} &= S_{iJ} F_{KJ} - \frac{qFC^f}{8\pi\epsilon |\mathbf{R}|} \left(\frac{\kappa + \det(\mathbf{F}) |\mathbf{R}|}{\det(\mathbf{F}) \kappa} \right) \exp \left(- \frac{\det(\mathbf{F}) |\mathbf{R}|}{\kappa} \right) H_{iK} \\
 &\quad - RT \sum_a (C^a - \det(\mathbf{F}) c_0^a) H_{iK}
 \end{aligned} \quad (2.54)$$

It is observed from the above material law (2.54) that the deformation of hydrogels is driven by osmotic pressure and repulsive force between fixed charges. Eqn. (2.54) with the mechanical field equation (2.45) characterizes how the hydrogel deforms when subjected to chemical and electrical effects.

2.3. MECis Model in One-Dimensional Domain

In this section, the 3-D MECis model is reduced to a one-dimensional domain for simplification.

In one-dimensional domain, the deformation gradient $\mathbf{F}$ could be reduced to

$$F_{11} = \lambda_1 = \frac{\partial x}{\partial X} = 1 + \frac{\partial u}{\partial X} \quad (2.55)$$

where u is the displacement, x and X are the Eulerian and Lagrangian coordinates in one-dimensional domain. F_{11} is the first component of deformation gradient, and λ_1 the stretching ratio in that direction. The determinant of the deformation gradient $\mathbf{F}$ is thus given as

$$\det(\mathbf{F}) = \lambda_1 = \frac{\partial x}{\partial X} \quad (2.56)$$

2.3.1. Chemical Field with Constitutive Flux

The 1-D form of the mobility tensor (2.14) is obtained as

$$M^a = \frac{D^a C^a}{\lambda_1^2} \quad (2.57)$$

Thus, the 1-D form of the constitutive flux (2.26) is given as

$$J^a = -\frac{D^a C^a}{\lambda_1^2} \left(\beta^a(\tilde{I}) \frac{\partial \tilde{I}}{\partial X} + \frac{\partial C^a}{\partial X} + \frac{z_a F}{RT} \frac{\partial \psi}{\partial X} \right) \quad (2.58)$$

Substituting the flux (2.58) into the chemical field equation (2.7), the chemical equation (2.7) is simplified to 1-D form as

$$\frac{\partial C^a}{\partial t} = \frac{D^a}{\lambda_1^2} \frac{\partial}{\partial X} \left(\beta^a(\tilde{I}) \frac{C^a \partial \tilde{I}}{\partial X} + \frac{\partial C^a}{\partial X} + \frac{z_a F}{RT} \frac{C^a \partial \psi}{\partial X} \right) + r^a \quad (2.59)$$

where the differential chain rule $\frac{d}{dX} \left(\frac{dX}{dx} \right) = \frac{d}{dx} \left(\frac{dX}{dX} \right) = 0$ is applied. The above

Eqn. (2.59) can be expanded to

$$\begin{aligned} \frac{\partial C^a}{\partial t} = & \frac{D^a}{\lambda_1^2} \left[\beta^a(\tilde{I}) \left(\frac{C^a \partial^2 \tilde{I}}{\partial X^2} + \frac{\partial C^a}{\partial X} \frac{\partial \tilde{I}}{\partial X} \right) + \frac{\partial^2 C^a}{\partial X^2} + \frac{z_a F}{RT} \left(\frac{C^a \partial^2 \psi}{\partial X^2} + \frac{\partial C^a}{\partial X} \frac{\partial \psi}{\partial X} \right) \right] + r^a \end{aligned} \quad (2.60)$$

2.3.2. Electric Field with Fixed Charge Equation

The 3-D electric field equation (2.34) is simplified to the 1-D form as

$$\frac{\varepsilon}{\lambda_1} \frac{\partial^2 \psi(X, t)}{\partial X^2} + F \left(z_f C^f(X, t) + \sum_b z_b C^b(X, t) \right) = 0 \quad (2.61)$$

The 3-D fixed charge equation (2.41) is simplified to the 1-D form as

$$C^f(X, t) = \frac{\phi_0^s C_{s,0}^f \tilde{K}_0 \exp \left[\alpha_4(z_b) \sqrt{\tilde{I}} / (1 + \alpha_2 \sqrt{\tilde{I}}) \right]}{\tilde{K}_0 \exp \left[\alpha_4(z_b) \sqrt{\tilde{I}} / (1 + \alpha_2 \sqrt{\tilde{I}}) \right] + C^b(X, t)} \quad (2.62)$$

2.3.3. Mechanical Field with Material Law

The 3-D Green strain tensor E_{iK} is simplified to the 1-D form as

$$E_{11} = \frac{\partial u}{\partial X} + \frac{1}{2} \left(\frac{\partial u}{\partial X} \right)^2 \quad (2.63)$$

For the isotropic Kirchhoff elasticity, the second Piola-Kirchhoff stress tensor in 1-D is written as

$$S_{11} = (l+2m) E_{11} = (l+2m) \left[\frac{\partial u}{\partial X} + \frac{1}{2} \left(\frac{\partial u}{\partial X} \right)^2 \right] \quad (2.64)$$

where l and m are Lamé's coefficients, and they are related to the Young's modulus E and Poisson's ratio ν in the forms of

$$l = \frac{\nu E}{(1 + \nu)(1 - 2\nu)}, \quad m = \frac{E}{2(1 + \nu)} \quad (2.65)$$

The 3-D material law (2.51) is simplified to the 1-D form as

$$P_{11} = F_{11} E_{11} - \frac{q F C^f}{8 \pi \varepsilon r} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) - \frac{R T}{\lambda_1} \sum_a (C^a - \bar{C}^a) \quad (2.66)$$

where r is the charge distance.

The 3-D mechanical field equation (2.45) is simplified to the 1-D form as

$$\begin{aligned} (l + 2m) \left[\frac{d^2 u}{dX^2} + 3 \frac{du}{dX} \frac{d^2 u}{dX^2} + \frac{3}{2} \left(\frac{du}{dX} \right)^2 \frac{d^2 u}{dX^2} \right] - \frac{R T}{\lambda_1} \sum_a \frac{\partial C^a}{\partial X} + B(X, t) \\ + \frac{q F C^f}{8 \pi \varepsilon \kappa} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \frac{\partial^2 x}{\partial X^2} - \frac{q F}{8 \pi \varepsilon r} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \frac{\partial C^f}{\partial X} = 0 \end{aligned} \quad (2.67)$$

2.4. Summary

In this chapter, the MECis model has been developed. It consists of three sets of governing equations and three sets of constitutive relations. The governing equations characterize the chemical, electrical and mechanical field variables, namely, the ionic concentrations, the electric potential and the displacement/stress. The constitutive equations include the flux, fixed charge density, and stress as functions of the ionic concentrations, deformation gradient, ionic strength and so on. The present model is based on four assumptions and simplifications. The first is that the diffusion coefficient is isotropic for both hydrogel and solution such that it can be represented by a scalar instead of tensor in the constitutive flux. The second is that the whole system is maintained in an isothermal condition, such that the flux driven by the gradient of temperature is negligible. The third is that the convection of the solvent is neglected, hence no fluid flow is considered during the swelling/shrinking. The last is that the dissociation and binding reactions are in local equilibrium, such that they are not influenced by adjacent reactions.

In the MECis model, the ionic strength plays a substantial role. It has significant influence not only on the flux directly via the activity coefficient as illustrated in Eqn. (2.26), but also on the fixed charge density via equilibrium constant and the repulsive force via the Debye length as illustrated in Eqs. (2.41) and (2.54) respectively. Furthermore, it also influences the concentration distribution of the ionic species indirectly and correspondingly the osmotic pressure. In brief, the present MECis model fully demonstrates the role of the ionic strength on the response of smart hydrogels.

The present model characterizes the responsive characteristics of the system physically in the following steps.

- Initially, the hydrogel and the solution system are in equilibrium, where the chemical and electric as well as mechanical fields are balanced.
- When ionic strength of the solution is changed, the mobile ions diffuse immediately into or out of the hydrogel. Meanwhile, the fixed charge groups of the hydrogel initiate the dissociation and the binding between the mobile ions and the fixed charges.
- The fixed charges formulate the electric field inside the hydrogel. In the solution, the different diffusion rates also result in the electric field.

- The electric field and the gradient of the ionic concentrations drive the mobile ions to diffuse further.
- The diffusion and the fixed charges lead to the difference of the ionic concentrations over the interface between the hydrogel and solution, which results in the osmotic pressure. Meanwhile, the electrostatic force is generated between the fixed charges.
- Both the osmotic pressure and electrostatic force drive the hydrogel to swell or shrink.
- The swelling and shrinking of the hydrogel result in the redistributions of the ionic concentration and fixed charge density as well as electric field. As such, the chemical, electrical and mechanical coupled fields are reformulated.
- The reformulation drives the mobile ions to diffuse again, and the hydrogel deforms further until the system reaches an equilibrium state.
- In the equilibrium state, the chemical, electrical and mechanical fields are balanced, where the gradients of the ionic strength, electric potential and concentration are equilibrated by each other, and the total fluxes of the mobile ions are equal to zero. The total charge density in the hydrogel is slightly deviates from zero, thus an electric potential exists. In addition, the elastic stretching of the hydrogel is balanced by the osmotic pressure and repulsive force.
- The equilibrium state remains until the environmental ionic strength is changed.

Fig. 2.1. The reference and current configurations for a hydrogel immersed in a solution.

3

Equilibrium Analysis of Ionic-Strength-Sensitive Hydrogel

3.1. Introduction

The equilibrium characteristics of the ionic-strength-sensitive hydrogel are of significance for applications of smart hydrogels in biosensors/bioactuators, microfluidic control and other hydrogel-based BioMEMS. Therefore, it is important to understand how the equilibrium characteristics influence the responsive deformation of the ionic-strength-sensitive hydrogel when immersed into the solution with different ionic strengths. As such, numerous studies have been performed experimentally and theoretically on the equilibrium of smart hydrogels (Goel *et al.*, 2006b; Hong *et al.*, 2010; Hooper *et al.*, 1990; Li *et al.*, 2008; Luo *et al.*, 2007; Ohmine and Tanaka, 1982).

In this chapter however, the equilibrium swelling and shrinking of ionic-strength-sensitive hydrogels are investigated using the steady-state MECis model. The objective of the investigation is not only to demonstrate the capability of the MECis model for simulation of the equilibrium characteristics of the ionic-strength-sensitive hydrogel, but also to carry out parametric studies of several important physical and chemical properties of the hydrogel and solution. It is noted that all the hydrogels analyzed in this chapter are limited to thin-disk geometric shape with diameters much larger than the thicknesses. Therefore, according to the classical 3-D elasticity theory, the deformation behavior of the hydrogel disks can be modeled as a 2-D plane-stress problem. In addition, the surrounding solution is generally in an isotropic unstirred condition without externally applied electric field, such that it is axis-symmetric about the centre of the plane-stress disk, and the problem can be further reduced to a 1-D domain along the radial direction of the disk.

Firstly, the numerical techniques are introduced in detail in order to implement the

simulation. After the nondimensional strategy of field variables is demonstrated, the one-dimension computational domain with the corresponding boundary conditions is defined. It is followed by the discretization in the spatial domain and the specified steady-state algorithm as well as the definition of the equilibrium swelling ratio.

After that, the examination of the MECis model is carried out via the one-dimensional steady-state simulation. The deformation behaviors of several ionic-strength-sensitive hydrogels, integrating different chemical, physical and mechanical properties, are analyzed using the MECis model. The simulation results are compared with past experimental and theoretical studies (Caykara and Dogmus, 2005; Dhara *et al.*, 1999; Hooper *et al.*, 1990; Okay *et al.*, 1998), and have validated the accuracy and robustness of the MECis model for equilibrium swelling/shrinking of ionic-strength-sensitive hydrogels.

Furthermore, the parameter studies are conducted systematically in order to obtain deeper insight into the underlying mechanism of equilibrium swelling/shrinking of hydrogels. The influence of the physical and chemical parameters on the swelling/shrinking behavior of ionic-strength-sensitive hydrogels under various conditions and the distribution of diffusive ion species and electric potential is investigated. The parametric studies include the influence of initial fixed charge density, equilibrium constant, Young's modulus, and initial fixed charge distance of the hydrogel. They characterize the properties of smart hydrogels and can be controlled when the hydrogel is synthesized.

3.2. Numerical Technique

In this section, the coupled nonlinear PDEs of the steady-state MECis model are first nondimensionalized and discretized using the Hermite-cloud method (Li *et al.*, 2003) mentioned earlier to analyze the equilibrium swelling/shrinking behavior of ionic-strength-sensitive hydrogels.

3.2.1. Nondimensional Implementation

In order to solve the MECis model efficiently, a set of dimensionless parameters are introduced as follows,

$$\bar{X} = \frac{X}{L_{ref}} \quad \bar{u} = \frac{u}{L_{ref}} \quad \bar{C}^a = \frac{C^a}{c_{ref}} \quad \bar{C}^f = \frac{C^f}{c_{ref}} \quad \bar{K}_0 = \frac{K_0}{c_{ref}} \quad \bar{\psi} = \frac{\psi}{\psi_{ref}} = \frac{F\psi}{\theta RT} \quad (3.1)$$

where $\bar{X}$, $\bar{u}$, $\bar{C}^a$, $\bar{C}^f$, $\bar{\psi}$ are the dimensionless variables of the coordinate, displacement, ionic concentration, fixed charge density, and electric potential, respectively. $L_{ref}(\text{m})$, $c_{ref}(\text{mol} / \text{m}^3)$, $\psi_{ref}(\text{V})$ and θ represent the references of the characteristic length, concentration, electric potential, and coefficient, respectively. As such, the dimensionless ionic strength $\bar{I}$ is given as

$$\bar{I} = \frac{1}{2} \sum_a z_a \bar{C}^a = \frac{\tilde{I}}{c_{ref}} \quad (3.2)$$

After nondimensionalization of Eqs. (2.60), (2.61), (2.62) and (2.67), the steady-state governing equations and constitutive relations are expressed as

$$\bar{\beta}^a(\bar{I}) \left(\frac{\bar{C}^a \partial^2 \bar{I}}{\partial \bar{X}^2} + \frac{\partial \bar{C}^a}{\partial \bar{X}} \frac{\partial \bar{I}}{\partial \bar{X}} \right) + \frac{\partial^2 \bar{C}^a}{\partial \bar{X}^2} + z_a \theta \left(\frac{\bar{C}^a \partial^2 \bar{\psi}}{\partial \bar{X}^2} + \frac{\partial \bar{C}^a}{\partial \bar{X}} \frac{\partial \bar{\psi}}{\partial \bar{X}} \right) = 0 \quad (3.3)$$

$$\frac{\varepsilon}{\lambda_1} \frac{\partial^2 \bar{\psi}(X)}{\partial \bar{X}^2} + \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} \left(z_f \bar{C}^f(X) + \sum_b z_b \bar{C}^b(X) \right) = 0 \quad (3.4)$$

$$\bar{C}^f(X) = \frac{\phi_0^s \bar{C}_{s,0}^f \bar{K}_0 \exp[\bar{\alpha}_4 \sqrt{\bar{I}} / (1 + \bar{\alpha}_2 \sqrt{\bar{I}})]}{\bar{K}_0 \exp[\bar{\alpha}_4 \sqrt{\bar{I}} / (1 + \bar{\alpha}_2 \sqrt{\bar{I}})] + \bar{C}^b(X)} \quad (3.5)$$

$$\begin{aligned} (l + 2m) & \left[\frac{d^2 \bar{u}}{d\bar{X}^2} + 3 \frac{d\bar{u}}{d\bar{X}} \frac{d^2 \bar{u}}{d\bar{X}^2} + \frac{3}{2} \left(\frac{d\bar{u}}{d\bar{X}} \right)^2 \frac{d^2 \bar{u}}{d\bar{X}^2} \right] \\ & + \frac{c_{ref} q F \bar{C}^f}{8\pi \varepsilon \kappa} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \left(\frac{\partial^2 \bar{u}}{\partial \bar{X}^2} \right) \\ & - \frac{c_{ref} q F}{8\pi \varepsilon r} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \frac{\partial \bar{C}^f}{\partial \bar{X}} - \frac{c_{ref} R T}{\lambda_1} \sum_a \frac{\partial \bar{C}^a}{\partial \bar{X}} = 0 \end{aligned} \quad (3.6)$$

where

$$\bar{\beta}^a(\bar{I}) = \left(\frac{-\bar{\alpha}_1 z_a^2}{\sqrt{\bar{I}} (1 + \bar{\alpha}_2 \sqrt{\bar{I}})^2} + \bar{\alpha}_3 \right) \quad (3.7)$$

with $\bar{\alpha}_2 = \alpha_2 \sqrt{c_{ref}}$, $\bar{\alpha}_3 = \alpha_3 c_{ref}$, $\bar{\alpha}_4 = \alpha_4 \sqrt{c_{ref}}$.

It is noted that the generative rate in the chemical field and body forces in the mechanical field are neglected here as they are not considered in this chapter.

3.2.2. Computational Domain and Boundary Condition

The present computational domain includes the regions of the hydrogel and

solution as well as hydrogel-solution interface. As mentioned before, a plane-stress hydrogel disk is considered, where the thickness dimension is much less than the radius, and boundary conditions are axis-symmetric. Therefore, only half of the domains of the hydrogel and external solution are considered as shown in Fig. 3.1, where the swelling/shrinking is 1-D isotropic along the radial direction without rotation.

In order to solve the governing equations, Dirichlet and/or Neumann boundary conditions are required, giving the prescribed field values and first-order derivatives respectively on domain edges. The present Dirichlet boundaries for chemical and electric fields are imposed at the edge of the solution, while the Neumann boundaries are applied at the center of the hydrogel due to the axisymmetry. For the mechanical field, the fixed boundary condition is required at the center of the hydrogel to avoid rigid-body motion, and the prescribed traction is applied at the hydrogel-solution interface due to the osmotic pressure. The boundary conditions for the three fields are thus given as

$$\begin{aligned}
 \left. \frac{\partial \bar{C}^a}{\partial \bar{X}} \right|_{\bar{X}=0} &= 0; & \left. \bar{C}^a \right|_{\bar{X}=1} &= c_0^a \quad (a = 1, 2, \dots) \\
 \left. \frac{\partial \bar{\psi}}{\partial \bar{X}} \right|_{\bar{X}=0} &= 0; & \left. \bar{\psi} \right|_{\bar{X}=1} &= 0 \\
 \left. \bar{u} \right|_{\bar{X}=0} &= 0; & P_{XX} N_X \big|_{X=L_{Gel}} &= T_0
 \end{aligned} \tag{3.8}$$

3.2.3. Discretization of Steady-State MECis Model

The dimensionless Eqs. (3.3) to (3.6) of the present MECis model are discretized by the Hermite-cloud technique for numerical solution (Li *et al.*, 2003), which is able to approximate the first-order derivative directly while achieving the same degree of computational accuracy with the field variable, and furthermore has less parameters compared to other meshless methods, as briefly introduced in Appendix B. There are several mathematical advantages for application of the Hermite-cloud method over other numerical methods in the present MECis model. For example, the local high gradient of the field variables over the interface between the hydrogel and solution, the easy treatment of moving boundary and the Dirichlet/Neumann boundary conditions, and remeshing of the computational domain.

By the Hermite-cloud method, the discretizations of the field variables are given by

$$\bar{C}^a(\bar{X}_i) = N_n(\bar{X}_i)\bar{C}_n^a + \left(\bar{X}_i - \sum_{n=1}^{N_P} N_n(\bar{X}_i)\bar{X}_n \right) M_m(\bar{X}_i)\bar{C}_{m,X}^a \quad (3.9)$$

$$\bar{\psi}(\bar{X}_i) = N_n(\bar{X}_i)\bar{\psi}_n + \left(\bar{X}_i - \sum_{n=1}^{N_P} N_n(\bar{X}_i)\bar{X}_n \right) M_m(\bar{X}_i)\bar{\psi}_{m,X} \quad (3.10)$$

$$\bar{u}(\bar{X}_i) = N_n(\bar{X}_i)\bar{u}_n + \left(\bar{X}_i - \sum_{n=1}^{N_P} N_n(\bar{X}_i)\bar{X}_n \right) M_m(\bar{X}_i)\bar{u}_{m,X} \quad (3.11)$$

where the subscript with the comma denotes the derivative with respect to the variable, $N_n(X)$ and $M_m(X)$ are the appropriate shape functions for the zero-order and first-order derivatives respectively by the Hermite-cloud methods, N_P and M_P are the numbers of the total scattered points in the domain for approximation of the zero-order and first-order derivatives, respectively, and $M_P \leq N_P$.

Accordingly, the first-order derivatives of the field variables are given by

$$\frac{\partial \bar{C}^a(\bar{X}_i)}{\partial \bar{X}} = M_m(\bar{X}_i)\bar{C}_{m,X}^a \quad (3.12)$$

$$\frac{\partial \bar{\psi}(\bar{X}_i)}{\partial \bar{X}} = M_m(\bar{X}_i)\bar{\psi}_{m,X} \quad (3.13)$$

$$\frac{\partial \bar{u}(\bar{X}_i)}{\partial \bar{X}} = M_m(\bar{X}_i)\bar{u}_{m,X} \quad (3.14)$$

and the second-order derivatives of the field variables are given by

$$\frac{\partial^2 \bar{C}^a(\bar{X}_i)}{\partial \bar{X}^2} = N_{n,XX}(\bar{X}_i)\bar{C}_n^a \quad (3.15)$$

$$\frac{\partial^2 \bar{\psi}(\bar{X}_i)}{\partial \bar{X}^2} = N_{n,XX}(\bar{X}_i)\bar{\psi}_n \quad (3.16)$$

$$\frac{\partial^2 \bar{u}(\bar{X}_i)}{\partial \bar{X}^2} = N_{n,XX}(\bar{X}_i)\bar{u}_n \quad (3.17)$$

As a result, the discretizations of the ionic strength could be expressed as

$$\bar{I}(\bar{X}_i) = \frac{1}{2} \sum_b z_b^2 \left[N_n(\bar{X}_i)\bar{C}_n^b + \left(\bar{X}_i - \sum_{n=1}^{N_P} N_n(\bar{X}_i)\bar{X}_n \right) M_m(\bar{X}_i)\bar{C}_{m,X}^b \right] \quad (3.18)$$

$$\frac{\partial \bar{I}(\bar{X}_i)}{\partial \bar{X}} = \frac{1}{2} \sum_b z_b^2 M_m(\bar{X}_i) \bar{C}_{m,X}^b \quad (3.19)$$

$$\frac{\partial^2 \bar{I}(\bar{X}_i)}{\partial \bar{X}^2} = \frac{1}{2} \sum_b z_b^2 N_{n,XX}(\bar{X}_i) \bar{C}_n^b \quad (3.20)$$

It is noted that n and m in the above equations are dummy indices and imply an addition over them.

After substituting Eqs. (3.9) to (3.20) into Eqs. (3.3) to (3.6), the governing and constitutive equations in the three fields are discretized in the form as

$$\begin{aligned} & \bar{\beta}^a(\bar{I}) \left[N_n(\bar{X}_i) \bar{C}_n^a + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^a \right] \\ & \times \left[\frac{1}{2} \sum_b z_b^2 N_{n,XX}(\bar{X}_i) \bar{C}_n^b \right] \\ & + \bar{\beta}^a(\bar{I}) \left[M_m(\bar{X}_i) \bar{C}_{m,X}^a \right] \left[\frac{1}{2} \sum_b z_b^2 M_m(\bar{X}_i) \bar{C}_{m,X}^b \right] + N_{n,XX}(\bar{X}_i) \bar{C}_n^a \\ & + z_a \theta \left[N_n(\bar{X}_i) \bar{C}_n^a + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^a \right] \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n \right] \\ & + z_a \theta \left[M_m(\bar{X}_i) \bar{C}_{m,X}^a \right] \left[M_m(\bar{X}_i) \bar{\psi}_{m,X} \right] = 0 \end{aligned} \quad (3.21)$$

$$\begin{aligned} & \frac{\varepsilon}{\lambda_1} \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n \right] + \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} z_f \bar{C}^f(X_i) + \\ & \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} \left\{ \sum_b z_b \left[N_n(\bar{X}_i) \bar{C}_n^b + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^b \right] \right\} = 0 \end{aligned} \quad (3.22)$$

$$\bar{C}^f(X_i) = \frac{\phi_0^s \bar{C}_{s,0}^f(X_i) \bar{K}(X_i)}{\bar{K}(X_i) + \left[N_n(\bar{X}_i) \bar{C}_n^b + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^b \right]} \quad (3.23)$$

where

$$\begin{aligned} & \bar{K}(X_i) = \\ & \bar{K}_0 \exp \left[\frac{\bar{\alpha}_4 \sqrt{\frac{1}{2} \sum_b z_b^2 \left[N_n(\bar{X}_i) \bar{C}_n^b + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^b \right]}}{\left(1 + \bar{\alpha}_2 \sqrt{\frac{1}{2} \sum_b z_b^2 \left[N_n(\bar{X}_i) \bar{C}_n^b + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^b \right]}} \right)} \right] \end{aligned} \quad (3.24)$$

$$\begin{aligned}
 & (l + 2m) \left\{ N_{n,XX}(\bar{X}_i) \bar{u}_n + 3 \left[M_m(\bar{X}_i) \bar{u}_{m,X} \right] \left[N_{n,XX}(\bar{X}_i) \bar{u}_n \right] \right\} \\
 & + \frac{3(l + 2m)}{2} \left[M_m(\bar{X}_i) \bar{u}_{m,X} \right]^2 \left[N_{n,XX}(\bar{X}_i) \bar{u}_n \right] \\
 & + \frac{c_{ref} q F \bar{C}^f(X_i)}{8\pi\epsilon\kappa} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp\left(-\frac{\lambda_1 r}{\kappa}\right) \left[N_{n,XX}(\bar{X}_i) \bar{u}_n \right] \\
 & - \frac{c_{ref} q F}{8\pi\epsilon r} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp\left(-\frac{\lambda_1 r}{\kappa}\right) \frac{\partial \bar{C}^f(X_i)}{\partial \bar{X}} - \frac{c_{ref} R T}{\lambda_1} \sum_b M_m(\bar{X}_i) \bar{C}_{m,X}^b = 0
 \end{aligned} \tag{3.25}$$

in which

$$\begin{aligned}
 & \frac{\partial \bar{C}^f(X_i)}{\partial \bar{X}} = \\
 & \frac{\phi_0^s \bar{C}_{s,0}^f(X_i) \bar{K}(X_i) \left[N_n(\bar{X}_i) \bar{C}_n^b + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^b \right]}{\left\{ \bar{K}(X_i) + \left[N_n(\bar{X}_i) \bar{C}_n^b + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^b \right] \right\}^2}
 \end{aligned} \tag{3.26}$$

The auxiliary equations required by the Hermite-cloud method are given by

$$N_{n,X}(\bar{X}) \bar{C}_n^a - (N_{n,x}(\bar{X}) \bar{X}_n) M_m(\bar{X}) \bar{C}_{m,X}^a = 0 \tag{3.27}$$

$$N_{n,X}(\bar{X}) \bar{\psi}_n - (N_{n,x}(\bar{X}) \bar{X}_n) M_m(\bar{X}) \bar{\psi}_{m,X} = 0 \tag{3.28}$$

$$N_{n,X}(\bar{X}) \bar{u}_n - (N_{n,x}(\bar{X}) \bar{X}_n) M_m(\bar{X}) \bar{u}_{m,X} = 0 \tag{3.29}$$

By the Hermite-cloud method, the Neumann boundary conditions Eqn. (3.8) are imposed as

$$0 = M_m(\bar{X}_0) \bar{C}_{m,X}^a \tag{3.30}$$

$$0 = M_m(\bar{X}_0) \bar{\psi}_{m,X} \tag{3.31}$$

$$\frac{T_0}{l + 2m} = M_m(\bar{X}_{MP}) \bar{u}_{m,X} \tag{3.32}$$

and the Dirichlet boundary conditions are imposed as

$$c_0^a = N_n(\bar{X}_{NP}) \bar{C}_n^a + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_{NP}) \bar{X}_n \right) M_m(\bar{X}_{NP}) \bar{C}_{m,X}^a \tag{3.33}$$

$$0 = N_n(\bar{X}_{NP}) \bar{\psi}_n + \left(\bar{X}_{NP} - \sum_{n=1}^{N_p} N_n(\bar{X}_{NP}) \bar{X}_n \right) M_m(\bar{X}_{NP}) \bar{\psi}_{m,X} \tag{3.34}$$

$$0 = N_n(\bar{X}_0) \bar{u}_n + \left(\bar{X}_0 - \sum_{n=1}^{N_p} N_n(\bar{X}_0) \bar{X}_n \right) M_m(\bar{X}_0) \bar{u}_{m,X} \tag{3.35}$$

Eqs. (3.21) to (3.35) coupled together constitute the whole nonlinear discrete system of the MECis model, on which the Newton-Raphson linearization is imposed in order to solve the nonlinear system numerically. The corresponding residuals of the governing equations are derived as

$$\begin{aligned}
 R_{chem}^a = & \bar{\beta}^a(\bar{I}) \left[N_n(\bar{X}_i) \bar{C}_n^a + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^a \right] \\
 & \times \left[\frac{1}{2} \sum_b z_b^2 N_{n,XX}(\bar{X}_i) \bar{C}_n^b \right] \\
 & + \bar{\beta}^a(\bar{I}) \left[M_m(\bar{X}_i) \bar{C}_{m,X}^a \right] \left[\frac{1}{2} \sum_b z_b^2 M_m(\bar{X}_i) \bar{C}_{m,X}^b \right] + N_{n,XX}(\bar{X}_i) \bar{C}_n^a \\
 & + z_a \theta \left[N_n(\bar{X}_i) \bar{C}_n^a + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^a \right] \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n \right] \\
 & + z_a \theta \left[M_m(\bar{X}_i) \bar{C}_{m,X}^a \right] \left[M_m(\bar{X}_i) \bar{\psi}_{m,X} \right]
 \end{aligned} \tag{3.36}$$

$$\begin{aligned}
 R_{elec} = & \frac{\varepsilon}{\lambda_1} \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n \right] + \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} z_f \bar{C}^f(X_i) \\
 & + \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} \left\{ \sum_b z_b \left[N_n(\bar{X}_i) \bar{C}_n^a + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^a \right] \right\}
 \end{aligned} \tag{3.37}$$

$$\begin{aligned}
 R_{mech} = & (l + 2m) \left\{ N_{n,XX}(\bar{X}_i) \bar{u}_n + 3 \left[M_m(\bar{X}_i) \bar{u}_{m,X} \right] \left[N_{n,XX}(\bar{X}_i) \bar{u}_n \right] \right\} \\
 & + \frac{3(l + 2m)}{2} \left[M_m(\bar{X}_i) \bar{u}_{m,X} \right]^2 \left[N_{n,XX}(\bar{X}_i) \bar{u}_n \right] \\
 & + \frac{c_{ref} q F \bar{C}^f(X_i)}{8 \pi \varepsilon \kappa} \left(\frac{\kappa + \lambda_1 r}{F_{11}^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \left[N_{n,XX}(\bar{X}_i) \bar{u}_n \right] \\
 & - \frac{c_{ref} q F}{8 \pi \varepsilon r} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \frac{\partial \bar{C}^f(X_i)}{\partial \bar{X}} - \frac{c_{ref} R T}{\lambda_1} \sum_b M_m(\bar{X}_i) \bar{C}_{m,X}^b
 \end{aligned} \tag{3.38}$$

$$R_{auxi}^a = N_{n,X}(\bar{X}) \bar{C}_n^a - \left(N_{n,x}(\bar{X}) \bar{X}_n \right) M_m(\bar{X}) \bar{C}_{m,X}^a \tag{3.39}$$

$$R_{auxi}^{elec} = N_{n,X}(\bar{X}) \bar{\psi}_n - \left(N_{n,x}(\bar{X}) \bar{X}_n \right) M_m(\bar{X}) \bar{\psi}_{m,X} \tag{3.40}$$

$$R_{auxi}^{mech} = N_{n,X}(\bar{X}) \bar{u}_n - \left(N_{n,x}(\bar{X}) \bar{X}_n \right) M_m(\bar{X}) \bar{u}_{m,X} \tag{3.41}$$

The incremental vector of the chemical, electrical and mechanical field variables and their first-order derivatives is defined as

$$\{\delta w\} = \begin{bmatrix} \delta \bar{C}^a \\ \delta \bar{\psi} \\ \delta \bar{u} \\ \delta \bar{C}_{,X}^a \\ \delta \bar{\psi}_{,X} \\ \delta \bar{u}_{,X} \end{bmatrix} \quad (3.42)$$

In the Newton-Raphson method, the Jacobian matrix is obtained by taking the derivatives of the residuals with respect to the field variables and their derivatives,

$$J_{ij} = \frac{\partial R_i}{\partial w_j} \quad (3.43)$$

where R_i is the i th residual function, and w_j is the j th field variable. The nonlinear discrete system thus becomes a linear algebra system and can be rewritten in matrix form as

$$J_{ij} \delta w_j = -R_i \quad (3.44)$$

After imposing the boundary conditions, the above linear algebra system is solved using a direct solver or other solvers. After each Newton iteration step, the solution is updated by

$$w_i^{q+1} = w_i^q + \delta w_i \quad (3.45)$$

where q is the iterative step. The iteration stops when the system reaches the convergence criterion

$$\frac{\max(\delta w_i)}{w_i^{q+1}} < \alpha \quad (3.46)$$

where α is the prescribed convergence criterion.

3.2.4. Steady-State Algorithm

Based on the Hermite-cloud and Newton-Raphson methods, the one-dimensional steady-state MECis model is solved numerically through the following procedures.

- (A). Inputting the physical and chemical parameters and boundary conditions;
- (B). Calculating the fixed charge density distribution;
- (C). Solving the chemical and electric fields at the coupled iteration step $n + 1$:

- a. Estimating solution $\bar{C}_{new}^a = \bar{C}_n^a$, $\bar{\psi}_{new} = \bar{\psi}_n$;

- b. Calculating the Jacobian matrix and right-hand side;
- c. Imposing the Dirichlet and/or Neumann boundary conditions;
- d. Solving $\Delta \bar{C}^a$ and $\Delta \bar{\psi}$;
- e. Updating solution, $\bar{C}_{new}^a \leftarrow \bar{C}_{old}^a + \Delta \bar{C}^a$, $\bar{\psi}_{new} \leftarrow \bar{\psi}_{old} + \Delta \bar{\psi}$;
- f. Checking the convergence criterion, if it is not met, go back to Step (C)b;
- (D). Calculating the osmotic pressure and electrical repulsive force;
- (E). Solving the mechanical field at the coupled iteration step $n + 1$:
 - a. Estimating next solution $\bar{u}_{new} = \bar{u}_n$;
 - b. Calculating the Jacobian matrix and right-hand side;
 - c. Imposing the Dirichlet and/or Neumann boundary conditions;
 - d. Solving $\Delta \bar{u}$;
 - e. Updating solution, $\bar{u}_{new} \leftarrow \bar{u}_{old} + \Delta \bar{u}$;
 - f. Checking the convergence criterion, if it is not met, go back to Step (E)b;
- (F). Updating the displacements, $u^{n+1} = u_{new}$;
- (G). Checking the convergence of u^{n+1} with u^n , if it is not met, updating counter, $n \leftarrow n + 1$, go back to Step (B);
- (H). Outputting the results.

After the convergence of the ionic concentration, electric potential, and displacement in each coupled iteration step, the convergence of displacement between the current and last coupled iteration steps is checked in order to ensure that the coupled chemical, electrical and mechanical fields have all converged.

3.2.5. Equilibrium Swelling Ratio

In this subsection, the equilibrium swelling ratio ESR is defined as the volume ratio of a hydrogel,

$$ESR = \frac{V}{V_0} \quad (3.47)$$

where V and V_0 are the volumes of the hydrogel in the equilibrium swollen and initial state respectively. The equilibrium swelling ratio ESR for the thin hydrogel disk can further be expressed as

$$ESR = \frac{\pi d^2 h / 4}{\pi d_0^2 h / 4} = \frac{d^2}{d_0^2} \quad (3.48)$$

where d and d_0 are the diameters of the swollen and initial hydrogel respectively, and h is the thickness of the disk.

In addition, the well-known hydration of the hydrogel H is another definition of the equilibrium swelling ratio, defined as the increment volume ratio below

$$H = \frac{V - V_0}{V_0} = \frac{d^2}{d_0^2} - 1 \quad (3.49)$$

In the subsequent sections, the above two definitions of the equilibrium swelling ratio are used according to the types of the hydrogel analyzed, when validating the MECis model by comparing the simulation results with the data from experiments and theories. For the parameter studies however, only the first definition ESR is employed.

3.3. Examination of the Steady-State MECis Model

In this section, the MECis model is examined for the equilibrium swelling ratio of the ionic-strength-sensitive hydrogel by comparing the MECis simulation results with published experimental data for four types of ionic-strength-sensitive hydrogels, namely poly[acrylamide(AAm)-*co*-acrylic-acid(AA)-poly(vinyl alcohol) (PVA)] (PAAP) hydrogel (Dhara *et al.*, 1999), poly(acrylamide-*co*-itaconic acid) (PAI) hydrogel (Caykara and Dogmus, 2005), poly[acrylamide(AAm)-*co*-2-acrylamideo-2-methylpropanesulfonic acide(AMPS)] (PAAS) hydrogel (Okay *et al.*, 1998), and poly-[AAm-*co*-[(methacrylamido)propyl]-trimethylammonium chloride] (PAMC) hydrogel (Hooper *et al.*, 1990). The comparison is also carried out with other theoretical results, such as the modified Flory-Rehner theory type-I and -II (Okay *et al.*, 1998), and gel-swelling model (Hooper *et al.*, 1990).

3.3.1. Comparison between MECis Model and Experiments

3.3.1.1 Equilibrium Swelling of PAAP Hydrogel

In the experimental work (Dhara *et al.*, 1999), the PAAP hydrogel was synthesized by acrylamide (AAm), acrylic acid (AA) and poly(vinyl alcohol) (PVA) with different

weight fractions of AAm and AA, and various PVA crosslinking time of 0, 5, 10, 20, 40 and 80 minutes, where the corresponding hydrogels were denoted as T0, T5, T10, T20, T40 and T80. In the PAAP hydrogel, the acrylic acid may dissociate in solution, the corresponding concentration is thus the fixed charge density and is calculated by

$$c_{AA} = \frac{\%AA / M_{AA}}{\%PVA / \rho_{PVA} + \%AAm / \rho_{AAm} + \%AA / \rho_{AA}} \quad (3.50)$$

where $\%AA$, $\%PVA$ and $\%AAm$ are the weight fractions of AA, PVA and AAm, respectively. $\rho_{AA}(1.052 \text{ g / cm}^3)$, $\rho_{PVA}(1.269 \text{ g / cm}^3)$ and $\rho_{AAm}(1.302 \text{ g / cm}^3)$ are the densities of AA, PVA and AAm, respectively. $M_{AA}(72.06 \text{ g / mol})$ is the molar mass of AA. Using Eqn. (3.50), the initial fixed charge density of PAAP is calculated and the values are equal to 881.7, 1753.7, 2600.6, and 3428.4mM for A1, A2, A3, A4 series of the hydrogel, respectively. The intrinsic dissociation constant of poly(acrylic acid) is $pK_0 = 3.6$ (Burke and Barrett, 2003; Vink, 1986). Young's moduli of PVA and poly(AAm-AA) measured by Martens *et al.* (2007) and Lopez-Ureta *et al.* (2008) respectively are employed in the present simulation. The dimension of the thin PAAP disk is $\phi 1.8 \times 0.6 \text{ cm}$, where ϕ denotes the diameter of the hydrogel disk. All the parameters used as input data for the simulation are summarized in Table 3.1.

The equilibrium swelling ratios ESR of the PAAP hydrogel via experiments and simulations are illustrated in Figs. 3.2 to 3.5 for A1, A2, A3 and A4 respectively. The figures demonstrate the comparison between experimental data and simulation results from the MECis model. The experimental data are represented by symbols, and the simulation results by lines. It is seen from the figures that the PAAP hydrogel shrinks with the increase of the ionic strength. The shrinking behavior of the PAAP hydrogel can be roughly separated into the three stages as follows. (1) Initially the swelling ratio decreases slowly, as the ionic strength of the solution increases to 1mM. (2) The hydrogel shrinks rapidly with the increase of the ionic strength ranging from 1mM to 100mM. (3) The swelling ratio remains almost constant or varies insignificantly when the ionic strength becomes larger than 100mM.

When the ionic strength is lower than 1mM, the ionic sodium is bound to the fixed charge sites since the valence of the fixed charge groups (AA) is -1 (Caykara and Dogmus, 2005). The bound reaction reaches the equilibrium state easily because of the

low ionic strength, and thus a lot of unbound fixed charges are still left on the polymeric chains. The unbound fixed charges attract the counterions into the interior hydrogel, which enlarges the osmotic pressure over the hydrogel-solution interface and then drives the hydrogel to swell drastically. A small change of the ionic strength influences the bound reaction unsubstantially at this stage, thus the number of fixed charges would not be affected much, which subsequently affects the osmotic pressure only slightly. In other words, if the environmental ionic strength is smaller than 1mM, the variation of the external ionic strength will alter the osmotic pressure insignificantly as the bound reaction is still active.

However, after an optimum binding for the ionic sodium to the polymer chains at the ionic strength of about 1mM (Caykara and Dogmus, 2005), the fixed charge sites are almost bound fully with the mobile ions and only a few unbound fixed charges are left, the further increase of the ionic strength in the solution reduces the osmotic pressure over the hydrogel-solution interface significantly, and thus the hydrogel shrinks drastically with the increase of the ionic strength from 1mM and 100mM.

When the environmental ionic strength is higher than 100mM, the hydrogel shrinks to a compact state, where almost no water or mobile ions exist in the hydrogel, the further increase of the ionic strength thus does not change the state of the hydrogel any more. In addition, the decrease of the ionic strength enlarges the Debye length, and this enhances the repulsive force. The increase of the ionic strength reduces the Debye length and then the effect of repulsive force on the swelling.

It is observed from the figures that the equilibrium swelling of the PAAP hydrogel decreases with the increase of the PVA crosslinking time. This is due to the strength improvement of the polymeric network with the increase of PVA crosslinking time. The increment of PVA crosslinking reaction time results in more PVA integrated into the PAAP hydrogel, and the polymeric chains crosslinkages become more complete, which restricts the segmental flexibility of the network. From the mechanical point of view, the increase of the crosslinked PVA improves the strength of the hydrogel. Therefore, the equilibrium swelling of the hydrogel decreases under the same environmental condition.

It is also observed from the figures that the predicted curves show the waviness, which mainly exists in the state when the swelling ratio is dropped or raised drastically. This type of waviness may result from computational errors, especially when the hydrogel changes the state rapidly from one equilibrium to another.

3.3.1.2 Equilibrium Swelling of PAI Hydrogel

The PAI hydrogel was synthesized experimentally with different mole ratios of AAm and itaconic acid (IA) (Caykara and Dogmus, 2005). The fixed charge densities with various compositions of AAm and IA are calculated by the concentration of IA which dissociates in solution, and the resulting values are given as 943, 2075.6 and 3459mM for PAI-1, PAI-2 and PAI-3, respectively. The initial distance between the fixed charges, also called as the mesh size, is determined by (Canal and Peppas, 1989)

$$r = Q^{1/3} \left(\frac{2\bar{M}_C}{M_r} \right)^{1/2} C_n^{1/2} l \quad (3.51)$$

where Q is volume swelling degree, l is C – C bond length and equal to 0.154 nm (Canal and Peppas, 1989), and C_n is a characteristic ratio of polymer which is calculated as the weighted average of the monomer values by

$$C_n = \frac{m_{AAm} C_n^{AAm} + m_{IA} C_n^{IA}}{m_{AAm} + m_{IA}} \quad (3.52)$$

In Eqn. (3.51), $\bar{M}_C$ is the average molecular weight of the polymer before crosslinking, and M_r the molecular weight of the repeating unit calculated by (Karadag *et al.*, 2001)

$$M_r = \frac{m_{AAm} M_{rAAm} + m_{IA} M_{rIA}}{m_{AAm} + m_{IA}} \quad (3.53)$$

The characteristic ratios of AAm and IA are obtained from the experiments of Kurata & Tsunashima (1989) and Veličković *et al.* (1994), and the average molecular weight values are obtained (Caykara *et al.*, 2004). By Eqs. (3.51) to (3.53), the initial charge distance of the three types of the PAI hydrogel are determined, equal to 30.7, 17.8 and 15.6nm for PAI-1, PAI-2 and PAI-3, respectively. The parameters used as input data for the simulation of the PAI hydrogel are tabulated in Table 3.2.

Fig. 3.6 shows the comparison of the simulation results with the experimental data (Caykara and Dogmus, 2005) for the PAI hydrogel. Similar to the PAAP hydrogel, the PAI hydrogel also possess the three stages of shrinking behavior because both share several common features. For instance, both the hydrogels incorporate the weak dissociation monomer (AA and IA) and are synthesized by AAm.

Furthermore, it is observed from the results that the increase of the initial fixed

charge density leads to the augmentation of the swelling ratio if the hydrogel is immersed in the solution with a given ionic strength. This is because the fixed charge groups dissociate in the solution and require the flux of water to ensure proper hydration of charged groups. With the increase in initial fixed charge density, more water and mobile ions penetrate into the interior hydrogel. The concentration of osmotic active ions thus increases inside the hydrogel, which enlarges the osmotic pressure over the hydrogel-solution interface and the hydrogel swells more. Meanwhile, the increase of fixed charge density in the hydrogel also enlarges the repulsive force contributed to the swelling.

As shown in Fig. 3.6, the simulation results of the PAI hydrogel are slightly deviates from experimental data (Caykara and Dogmus, 2005) when the ionic strength ranges from 0.01 to 0.1 M. A probable reason is the dissociation constant. In the present comparison, the dissociation constant of the itaconic acid is used as that of PAI hydrogel. Perhaps the copolymer of AAm and IA affects the dissociation constant of IA, since the dissociation behavior of polymer is influenced by the short-range electrostatic interaction between the charges, charge density, and structure of the network (Kawaguchi *et al.*, 1990). From the present simulation result, it is estimated that the dissociation constant of PAI is less than that of IA, since the predicted equilibrium swelling ratios are less than the experimental data.

3.3.1.3 Equilibrium Swelling of PAAS Hydrogel

The PAAS hydrogel was prepared by acrylamide (AAm) and 2-acrylamideo-2-methylpropanesulfonic acid (AMPS) monomers, with *N, N'*-methylenebis(acrylamide) as the crosslinker (Okay *et al.*, 1998). As AMPS is a strongly dissociating monomer, it is considered as the fixed charge groups in the hydrogel. The initial fixed charge densities are obtained and equal to 0, 47, 94, 140, 276mM, corresponding to the mole fraction of AMPS of 0, 0.25, 0.5, 0.75, 1.5%, respectively. Since AMPS can be dissociated strongly in aqueous solution, the binding constant of AMPS is used in this simulation (Kasseh and Keh, 2006). The reason is that, for weakly dissociated hydrogel, the binding process between the hydrogel and mobile ions is mainly restricted by the dissociation of the hydrogel. For strongly dissociated hydrogel, however, the binding reaction of the counterions is mainly dependent on the binding constant. The mole fraction of AMPS is very small in the four hydrogels, such that the

effect of AMPS on Young's modulus and initial charge distance of the hydrogel can be neglected. All the parameters used as input data for the simulation are listed in Table 3.3.

The equilibrium swelling ratio *ESR* by the MECis model and the experimental data for PAAS (Okay *et al.*, 1998) is depicted in Fig. 3.7. As observed from the figure, the PAAS hydrogel also possess the shrinking behavior with the increase of the ionic strength of the solution. However, the shrinking can be separated into two phases. The first is that the hydrogel shrinks drastically if the ionic strength is lower than 10mM, and the second is that the hydrogel almost remains in a compact state or changes slightly thereafter. The different behavior of shrinking for PAAS hydrogel may be due to the strong dissociation of the AMPS monomer in solution. The characteristic of strong dissociation property makes the bounding of sodium ions to the fixed charge sites difficult. Therefore, it is relatively easy to reach the optimum binding as the binding reaction is in equilibrium even when the ionic strength is very low, e.g., below 0.1mM. After the optimum binding, the increase of the ionic strength reduces the osmotic pressure over the hydrogel-solution interface and thus the hydrogel shrinks. When the hydrogel shrinks to an almost compact state, the further increase of the ionic strength will no longer change the equilibrium swelling ratio.

It is also observed from Fig. 3.7 that the hydrogel swells more significantly if it incorporates more amounts of AMPS. The reason may come from the fact that the higher the mole percentage of AMPS incorporated, the more fixed charges are produced on the crosslinked chains of the hydrogel, which attracts more counterions and thus develops larger osmotic pressure and repulsive force. These result in greater swelling ratio at equilibrium.

3.3.1.4 Equilibrium Swelling of PAMC Hydrogel

The PAMC hydrogel was synthesized by AAm and [(methacrylamido)propyl]-trimethylammonium chloride (MAPTAC) with *N, N'*-methylenebis(acrylamide) (BIS) as the crosslinker (Hooper *et al.*, 1990). The composition of the hydrogel was characterized by three variables, %C (the mole percentage of crosslinking monomer), %T (the ratio of all the monomer mass to volume of water), and M% (the mole percentage of MAPTAC). Since MAPTAC is positive charged, it is therefore the fixed charges in the hydrogel. Three types of the hydrogels were synthesized by different

compositions, i.e., varying the above three variables. By fixing %C = 0.2, %M = 2.0 and varying %T = 15, 20, 25, the three T-series of PAMC hydrogels were prepared. The initial fixed charge densities for the T-series of hydrogels are thus obtained as 343, 457 and 572mM respectively. By fixing %T = 15, %M = 2.0 and varying %C = 0.1, 0.2, 0.5, 1, 5, the five C-series of the PAMC hydrogels were prepared. The initial fixed charge densities for the C-series of hydrogel are calculated as 343, 343, 343, 340 and 325mM accordingly. By fixing %T = 15, %C = 0.2, and varying %M = 0, 1, 2, 3, 4, 5, the six M-series of PAMC hydrogels were synthesized. The initial fixed charge densities for the six M-series of hydrogels are calculated as 0, 175, 343, 504, 660, 810mM accordingly. In all the hydrogels prepared, the major composition was AAm, thus the initial charge distance and Young's modulus of AAm were used. Since the PAMC hydrogel is positive charged after the dissociation of MAPTAC, the chlorine ions binds to the fixed charge sites. All the input data required by the MECis model are listed in Table 3.4 for T-series, Table 3.5 for C-series, and Table 3.6 for M-series of PAMC.

The equilibrium swelling ratio *ESR* for the PAMC hydrogel is presented in Figs. 3.8, 3.9 and 3.10 for T-, C- and M-series respectively (Hooper *et al.*, 1990), in which the symbols represent the experimental data, and the solid lines the corresponding MECis results. The shrinking behavior of the PAMC hydrogel can also be separated into two phases like the PAAS hydrogel with the increase of the ionic strength, since they both incorporate strong dissociation monomers (AMPS and MAPTAC).

It is shown in Fig. 3.8 that the amount of total monomers has substantial influence on the PAMC hydrogel. In the same volume, larger amount of monomers actually increases the crosslinking strength, which makes the hydrogel structure more compact and rigid, thus reducing the flexibility of the hydrogel. The polymeric chains are restricted with more adjacent chains. This leads to difficulty for the chains to move or rotate, and consequently the deformation of the hydrogel in macroscopic view. Therefore, the equilibrium swelling of the T-series of hydrogels reduces with an increase in the amount of total monomers.

The C-series of PAMC hydrogel possess the similar properties with the increase of the amount of the crosslinking monomers (%C), as shown in Fig. 3.9. The crosslinking monomers as activators influence the crosslinking efficiency. As the amount of the crosslinking monomers increases, more polymeric chains are crosslinked with one another in a limited period of time. The flexibility of the polymeric chains is thus

reduced and the network strength is enhanced. The equilibrium swelling ratio of the C-series hydrogel is therefore decreased with an increment of crosslinking monomers.

The MECis model predicts well the behavior of the PAMC hydrogel with an increase of the crosslinking monomers and total monomers. In the MECis model, the network strength is characterized by the macro variable, i.e., Young's modulus. By the above comparison, it is concluded that the elastic behavior of the hydrogel network is well handled by the mechanical field in the MECis model.

Fig. 3.10 shows that the PAMC hydrogel swells more significantly with increasing the content of MAPTAC. As discussed above, the dissociation of MAPTAC leaves the positive charges fixed on the polymeric network chains, and it thus determines the fixed charge density of the PAMC hydrogel. The influence of the initial fixed charge density on the swelling ratio of the PAMC hydrogel is mainly due to the binding reaction between chlorine ions and the fixed charges. For a given binding constant, the larger number of initial fixed charges leaves more unbound fixed charges, which attracts more counterions to the polymeric network, thus producing a larger concentration difference and in turn a higher osmotic pressure. Therefore, the hydrogel expands much more to reach the equilibrium state. However, when the ionic strength of environmental solution is larger than 100mM, the hydrogel remains in a compact state, thus the effect of the initial fixed charge density becomes insignificant on the swelling ratio.

3.3.2. Comparison between MECis Model and Other Theories

3.3.2.1 Modified Flory-Rehner Theory

The modified Flory-Rehner theory considers the three contributions to the swelling pressure Π , namely the polymer/solvent mixing Π_{mix} , the elastic deformation of the network chains Π_{ela} , and ionic contribution due to the presence of mobile and bound ions Π_{ion} . When the hydrogel is equilibrated with the solvent, the equilibrium of thermodynamics gives

$$\Pi = \Pi_{mix} + \Pi_{ela} + \Pi_{ion} = 0 \quad (3.54)$$

The mixing pressure Π_{mix} is determined by the Flory-Huggins theory as

$$\Pi_{mix} = -\frac{RT}{V} \left(\ln(1 - v_2) + v_2 + \chi v_2^2 \right) \quad (3.55)$$

where v_2 is the volume fraction of polymer in the hydrogel, χ is the polymer–solvent interaction parameter. The elastic pressure Π_{ela} is given as

$$\Pi_{ela} = -\frac{RT}{V} N_s^{-1} \left[v_2^{1/3} (v_2^0)^{1/3} - \frac{v_2}{2} \right] \quad (3.56)$$

where N_s is the average number of segments in the polymeric network chain, and v_2^0 is the volume fraction of the polymer network at reference state. The ionic contribution Π_{ion} due to the osmotic pressure is given as

$$\Pi_{ion} = RT \sum_i (c_i^{gel} - c_i^{ext}) \quad (3.57)$$

where c_i^{gel} and c_i^{ext} are the ionic concentrations within the gel and the external solution. The ionic concentration is determined by

$$c_+^{gel} c_-^{gel} = (c_s^{ext})^2 \quad (3.58)$$

$$c_+^{gel} = c_-^{gel} + c^{fix} \quad (3.59)$$

where c^{fix} is the fixed charge density. Here, only the monovalent solution and fixed charges are considered. The fixed charge density is calculated by

$$c^{fix} = \frac{f}{V_r} v_2 \quad (3.60)$$

where f is the mole fraction of charged units in the network, and V_r the molar volume of the polymer repeat unit. By Eqs. (3.54) to (3.60), one obtains (Okay *et al.*, 1998)

$$\begin{aligned} \ln(1 - v_2) + v_2 + \chi v_2^2 + N^{-1} \left[v_2^{1/3} (v_2^0)^{2/3} - v_2 / 2 \right] \\ - 2(K - 1) V c_s^{ext} - V c^{fix} = 0 \end{aligned} \quad (3.61)$$

$$K(K + c^{fix} / c_s^{ext}) - 1 = 0 \quad (3.62)$$

where $K = c_-^{gel} / c_s^{ext}$, and c_s^{ext} is the concentration of charge in the solution. By assuming $c_s^{ext} = 0$ for nonionic solution, Eqs. (3.61) and (3.62) are rewritten as

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + N^{-1} \left[v_2^{1/3} (v_2^0)^{2/3} - v_2 / 2 \right] - V c^{fix} = 0 \quad (3.63)$$

In Eqs. (3.61) to (3.63), there are four unknowns, N , f , c_-^{gel} and v_2 , to be determined but cannot be solved unless one of them is known. There are two different methods to determine N or f , namely the fixed crosslink density N , and varied charge density f . (Okay *et al.*, 1998).

Using $v_2 = 1 / 40.09$ for nonionic gel and $c_-^{fix} = 0$, Eqn. (3.63) is solved as $N = 1.2 \times 10^3$. By this fixing crosslink density N , the three Eqs. (3.61)-(3.63) are solved and the swelling ratio $1 / v_2$ is obtained. This is the modified Flory-Rehner theory-I.

Alternatively, by assuming that AMPS is completely dissociated, the charge density f in the reference state can be calculated by (Okay *et al.*, 1998)

$$f = \frac{\text{AMPS mol \%}}{100} \quad (3.64)$$

Accordingly, for different f , Eqs. (3.61)-(3.63) can be solved, and the swelling ratio $1 / v_2$ is obtained. This is the modified Flory-Rehner theory-II.

As shown in Fig. 3.7, the predicted equilibrium swelling ratio is compared with the modified Flory-Rehner theory-I (fixed crosslink density) illustrated by blue dash line, and with the modified Flory-Rehner theory-II (fixed charge density) by magenta dot line, where the simulation results by the MECis model are denoted by solid lines. It is observed that the MECis model agree well with both the Flory-Rehner theories.

In the MECis model, the effects of the chemical, electrical and mechanical energy domains are coupled. In the Flory-Rehner theory, however, the four parameters, including the polymer-solvent interaction parameter, the number of the segments, the charged unit in the networks, and the salt concentration of external solution, are included without consideration of electrical and mechanical effects. In addition, there are three main differences between the MECis model and Flory-Rehner theories. The first is that the Flory-Rehner theory does not consider the equilibrium reaction between the fixed charge groups and mobile ions in the solution. The second is that the interaction of mobile ions, such as the electrophoresis, is not included in the Flory-Rehner model. The third is that Flory-Rehner theory does not consider the interaction between the fixed charges which influences the swelling of the hydrogel; it only considers the elastic deformation. It is pointed out that all the three effects that are not considered by the Flory-Rehner theory are included in the present MECis model.

However, it is demonstrated by the above comparisons that the description of the swelling of the hydrogel by both the present MECis model and the Flory-Rehner theory may approach to each other.

3.3.2.2 Gel-Swelling Theory

The gel-swelling theory is an extension or modification of the Flory-Rehner theory (Hooper *et al.*, 1990), in which the swelling pressure Π also comes from the three contributions as in Eqn. (3.54), with different explanations of the three contributions.

The mixing pressure Π_{mix} is written as

$$\begin{aligned} \Pi_{mix} = & -\frac{RT}{V} \left[\ln \phi_1 + \phi_2 - \frac{1}{2} z_1^\alpha q_1 \ln \left[\frac{\Gamma_{11,pure}^{\alpha\alpha}}{\Gamma_{11,mix}^{\alpha\alpha}} \right] \right] \\ & - \frac{RT}{V} \left[\frac{1}{2} z_1^\beta q_1 \ln \left[\frac{\Gamma_{11,pure}^{\beta\beta}}{\Gamma_{11,mix}^{\beta\beta}} \right] + \frac{1}{2} z_1^D q_1 \ln \left[\frac{\Gamma_{11,pure}^{DD}}{\Gamma_{11,mix}^{DD}} \right] \right] \end{aligned} \quad (3.65)$$

where ϕ_1 and ϕ_2 represent the volume fraction of the solvent and polymer in the gel, q_1 and z_1 are structural parameters of the solvent, and Γ_{11} is a factor representing the extent of nonrandom mixing around each type of contact site on the solvent. In this model, each solvent molecule or polymer segment may have one, two, or three types of interaction sites, namely the hydrogen-bond donating sites (α sites), hydrogen-bond accepting sites (β sites), and sites that interact through dispersion forces (D sites) (Hooper *et al.*, 1990).

The elastic contribution Π_{ela} is based on the constraint theory,

$$\Pi_{ela} = -\frac{1}{2} \frac{RT}{V} \left(\frac{\phi_2^0}{x_c} \right) \left[(1 - F) + (2 - \lambda^{-2})F \right] \quad (3.66)$$

where ϕ_2^0 is the volume fraction of the gel in the reference state, x_c denotes the average number of segments per network chain, λ the dilation ratio $\lambda = (\phi_2^0 / \phi_3)^{1/3}$, and F varies between 0 (no constraints on junctions) and 1 (complete constraints on junctions). Eqn. (3.66) is the weight average of the affine and phantom theories (Hooper *et al.*, 1990).

The ionic contribution Π_{ion} due to the osmotic pressure is given by Eqn. (3.57), and the ionic concentration obeys the Donnan equilibrium as

$$\left(\frac{c_s^{gel}}{c_s^{ext}} \right) = \frac{c_s^{ext}}{c_s^{gel} + \frac{i\phi_2}{V_m}} \quad (3.67)$$

where c_s^{gel} refers to the concentration of salt within the gel and c_s^{ext} the concentration of salt in the surrounding solution, i represents the fraction of monomer units containing bound charges, and V_m denotes the molar volume of a monomer unit.

Figs. 3.8 to 3.10 show the theoretical results by the MECis and by the gel-swelling models (Hooper *et al.*, 1990), respectively, where the solid line is for MECis results, and the dash line for gel-swelling model. It is observed from the figures that it is difficult for the gel-swelling model to accurately predict the effect of the total monomers and the crosslinking monomers on the equilibrium swelling behavior of the ionic-strength-sensitive hydrogel, especially in the low ionic strength solution. However, the present MECis model is able to handle simulations well, not only for the response of swelling behavior of the hydrogel to ionic strength, but also for analysis of the influence of total and crosslinking monomers.

In addition, it is noted that the gel-swelling model does not consider the effect of the equilibrium reaction between the fixed charge and mobile ions, and the repulsive force. Although the constrained junction theory is used to describe the elastic contribution on the chemical potential, the influence of the polymeric structure on the strength of the hydrogel is not fully considered. Therefore, the gel-swelling model is not sensitive to the variation of the total monomer (T%) and crosslinking monomers (C%). In MECis model, however, the strength of the hydrogel reflects the structure of the hydrogel at macroscopic scale. Experiments show that the total monomer concentration and the ratio of crosslinking agent influence the strength of the hydrogel to a large extent (Baker *et al.*, 1994; Saeidi *et al.*, 2004). The strength of hydrogel is considered in MECis model based on a mechanical theory, where Young's modulus of the hydrogel increases with the increase of the total monomer concentration and amount of crosslinking agent. Therefore, the MECis model can predict the influence of the total monomer concentration and amount of crosslinking agent on the swelling ratio of the ionic-strength-sensitive hydrogel accurately.

3.3.3. Remarks

The above comparisons and discussions show that the MECis model can work well for good prediction of the equilibrium swelling ratios of the ionic-strength-sensitive hydrogel, with a good agreement with the experimental data. It is also observed that the MECis model is able to approach to the classic Flory-Rehner theory well, even to obtain better result than that of the Flory-Rehner model. Therefore, it can be concluded with confidence that the present MECis theory is capable of modeling the equilibrium swelling/shrinking of the ionic-strength-sensitive hydrogel and the responsive characteristics of diffusive ion species and electric potential.

3.4. Parameter Studies

In general, computational modeling via the parameter study is more cost efficient compared with experimental approaches. In order to improve the understanding of the influence of various environmental conditions or physical and chemical material parameters on the equilibrium characteristics of the hydrogel, four parametric studies are carried out in this section for design and optimization of the ionic-strength-sensitive hydrogel. They include the initial fixed charge density, the equilibrium constant, Young's modulus and the initial fixed charge distance of the hydrogel.

3.4.1. Influence of Initial Fixed Charge Density

Usually the ionizable pendent groups are bound on the polymeric chains and dissociate partially or completely when the hydrogel is immersed into solution. If the pendent groups are ionized, the charges are bound on the polymeric chains, which are termed the fixed charge groups. Deformation behavior of the ionic-strength-sensitive hydrogel is much dependent on the fixed charge density because the ionic interaction between the mobile ions and fixed charges makes great contribution to the osmotic pressure over the hydrogel-solution interface. In addition, the electrostatic force between the fixed charges, which is called the repulsive force, is also an important driving source for expansion of the hydrogel. As such, these two effects of the fixed charge density have to be considered in the analysis of performance of the ionic-strength-sensitive hydrogel for design and optimization of the hydrogel-based

bio-device. Furthermore, the fixed charge density is changed with the deformation of the hydrogel, because of the ionic interaction between the mobile ions and fixed charges. Therefore, the initial fixed charge density is investigated in details in this subsection since it is an important chemical property of the hydrogel.

Regarding the effect of the initial fixed charge density on the ionic-strength-sensitive hydrogel, so far few theoretical studies have been done. For example, Hooper *et al.* (1990) presented a gel-swelling model to describe the effect of the fixed charge density on the swelling ratio of the positively ionized polyacrylamide hydrogel. Baker *et al.* (1995) analyzed the influence of gel net charge on the swelling ratio by incorporating the Debye-Huckel theory into a Flory swelling model. Okay *et al.* (1998) improved the Flory-Rehner theory to predict the responding behavior of the ionic-strength-sensitive hydrogel with different fixed charge densities, and concluded that the theory could correctly predict the swelling of the hydrogel with low and medium charge density. Li *et al.* (2006a) presented a model for the ionic-strength-sensitive hydrogel based on the Flory-Rehner theory, and found that the volume swelling ratio increased with the square of fixed charge density and the reciprocal of ionic strength. However, most of the above models do not consider the interaction between the mobile ions and fixed charge, although they include the effect of the fixed charge on the electroneutrality condition in the hydrogel.

In order to gain a deeper insight into the effect of the initial fixed charge density on the characteristics of the ionic-strength-sensitive hydrogel, the parameter study is carried out by the MECis model for analysis of the ionic transport, the distribution of electric potential, the fixed charge density and the displacement. The representative input data required by the MECis model include: the gel radius $L_{gel} = 2\text{mm}$, the whole computational domain length $L = 10\text{mm}$, the valence of the fixed charge $z_f = -1$, Young's modulus $E = 0.9\text{MPa}$, the initial distance between the fixed charges $r_0 = 60\text{nm}$, the intrinsic dissociation constant $K_0 = 10^{-3.6}$, the temperature $T = 298\text{K}$. The initial fixed charge densities are given as $C_0^f = 600, 1200, 1800, 2400\text{mM}$ in simulation for parameter studies. The analysis of the effect of the initial fixed charge density on the characteristics of the ionic-strength-sensitive hydrogel is carried out for two different ionic strengths of the environmental solution, namely 1mM and 100mM, as examples of low and high ionic

strengths respectively.

Fig. 3.11 demonstrates the effect of the initial fixed charge density C_0^f on the normalized equilibrium swelling ratio ESR of the hydrogel subject to different environmental ionic strengths. Compared with the small change of the equilibrium swelling ratios ESR at high ionic strength, ESR increases drastically at low ionic strength with the increase of the initial fixed charge density C_0^f . This is due to the presence of the initial fixed charge requiring counterions to maintain the electroneutrality inside the hydrogel. Then the concentration of osmotic active ions increases inside the hydrogel, resulting in the increase of the osmotic pressure over the hydrogel-solution interface. Meanwhile, the larger number of the fixed charges on the polymeric chains within the hydrogel produces the larger repulsive force between the fixed charges, which also contributes to the equilibrium swelling ratio ESR , especially at low ionic strength. At high ionic strength however, the equilibrium swelling ratio ESR is determined mainly by the osmotic pressure that changes slightly with the initial fixed charge density C_0^f , since the large number of mobile ions in the hydrogel shields the effect of the fixed charges on the repulsion.

The distributive profiles of the fixed charge density C^f at the equilibrium state are provided in Figs. 3.12(c) and 3.13(c) for the low (1mM) and high (100mM) environmental ionic strengths, respectively. The fixed charge density C^f at swollen state is less than that at the initial state due to the interaction between the fixed charges and mobile ions, and the volume increase of the hydrogel. It is observed from the figures that the fixed charge density C^f after swelling increases with the growth of the initial fixed charge density C_0^f , no matter at low or high ionic strengths. This is obvious since the larger initial fixed charge density C_0^f leaves more unbound fixed charges at a given ionic strength, after bound mobile counterions. It is also found that the increment of the fixed charges becomes narrow with the same interval between adjacent initial fixed charge densities if the ionic strength is 1mM. At high ionic strength however, the increment of the fixed charge density remains almost the same. This may result from swelling of the hydrogel. In the solution with high ionic strength, e.g., 100mM, the hydrogel always keeps a compact state, the swelling ratio of the hydrogel is not affected much by the initial fixed charge density. Thus the increment of

the fixed charge density after binding reaction is the same as the increment of the initial fixed charge density. However, in the solution with low ionic strength, e.g., 1mM, the equilibrium swelling ratio of the hydrogel is influenced by the initial fixed charge density C_0^f because of the activity of the binding reaction. With higher initial fixed charge density C_0^f , the hydrogel swells more and then the volume of the hydrogel increases further. Therefore, the increment change of the fixed charge density decreases.

Figs. 3.12(a) and 3.13(a) illustrate the equilibrium distributive concentration of positive ions C^+ within the external solution and hydrogel with various initial fixed charge densities C_0^f , when immersed in the solution with low (1mM) and high (100mM) ionic strengths, respectively. It is seen that the concentration of the positive ions C^+ inside the hydrogel rises with the increase of the initial fixed charge density C_0^f , no matter at low or high ionic strength of the solution. In the external solution however, the concentration of the positive ions C^+ is not changed by the different initial fixed charge densities C_0^f . It is known that the larger initial fixed charge density C_0^f leaves more unbound fixed charges at the swollen state. The left unbound fixed charges attract the positive ions and repel the negative ions to maintain the electroneutrality inside the hydrogel, which leads to the increase of the concentration of the positive ions C^+ in the interior hydrogel. It is also observed from the figures that the increment of the positive ions inside the hydrogel reduces even if the initial fixed charge density C_0^f increases in the same degree when the hydrogel is immersed into the solution with low ionic strength. However, in the solution with high ionic strength, the equal increment of the positive ionic concentration is observed due to the unbound fixed charges in the hydrogel.

Figs. 3.12(b) and 3.13(b) demonstrate the variation of equilibrium concentration of the negative ions C^- in the external solution and interior hydrogel with different initial fixed charge densities C_0^f , when immersed in the solution with the ionic strengths of 1mM and 100mM respectively. It is observed that, with the increase of the initial fixed charge density C_0^f , the concentration of the negative ions C^- decreases in the interior hydrogel and almost remains unchanged in the external solution. The

concentration of the negative ions C^- is determined by the unbound fixed charges, which repel the negative ions out of the hydrogel to maintain the electroneutrality since the valence of the unbound fixed charges in the hydrogel is taken as -1 here. Similar to the concentration of the positive ions C^+ , the decrease interval of the concentration of the negative ions C^- also becomes narrow when the initial fixed charge density C_0^f increases for the solution with low ionic strength and almost keeps the same degree for the solution with high ionic strength.

Figs. 3.12(d) and 3.13(d) exhibit the equilibrium distribution of electric potential ψ in the interior hydrogel and external solution. A slight difference between the various ionic concentrations results in a constant electric potential inside the hydrogel and is usually very small. In the external solution however, the electric potential is zero and the electroneutrality exists due to the summation of the total concentrations of all the ionic species. It is shown in Figs. 3.12(e) and 3.13(e) that the displacements u of the hydrogel are distributed linearly and the displacement drops with the decrease of the initial fixed charge density. The displacements u become larger when the hydrogel is immersed into solution with low ionic strength than those with high ionic strength. The existence of the initial fixed charge density C_0^f produces the osmotic pressure over the hydrogel-solution interface and thus the displacement of the hydrogel u . However, the high ionic strength of the bath solution holds the growth of the displacement u , thus the equilibrium swelling ratio ESR of the hydrogel is induced by the difference in initial fixed charge densities C_0^f . At low ionic strength, the disparity of the osmotic pressure and repulsion caused by the different initial fixed charge densities C_0^f is very large. The driving force is equilibrated by the internal stress of the hydrogel and thus it produces strain. The large difference of driving forces also induces the large disparity of internal stress due to different fixed charge densities C^f , which makes the difference of displacement u . In contrast, the high ionic strength of the bathing solution confines the variation of the osmotic pressure and repulsion with different initial fixed charge densities C_0^f of the hydrogel, and thus the small variance of driving forces could not make much difference of internal stresses which restrict the change of displacement.

In summary, it is concluded that the initial fixed charge density C_0^f significantly

influences the equilibrium swelling ratios ESR at low ionic strength. At high ionic strength however, ESR remains virtually the same no matter how the initial fixed charge density C_0^f changes. The different initial fixed charge densities C_0^f also affect the ionic concentrations and electrical potential inside the hydrogel appreciably due to the electroneutrality.

3.4.2. Influence of Equilibrium Constant

The equilibrium constant of the hydrogel is one of the most important parameters, as it affects the swelling behavior of the hydrogel through the equilibrium reaction between fixed charges and mobile ions. As is well known, the equilibrium constant K could be changed experimentally by incorporating different ionizable groups, cooperative binding, and/or strong interaction between binding sites. For consideration of the effect of the equilibrium constant on the swelling behavior of the smart hydrogel responsive to the ionic strength, Brannon-Peppas and Peppas proposed a model based on the Flory-Huggins thermodynamics theory and the rubber elasticity theory (Brannon-Peppas and Peppas, 1991b), in which the ionization of the hydrogel is determined by the dissociation constant and the pH value of bathing solution, and thus the ionic contribution to the swelling is obtained by the ionization. They applied the model for analysis of the influence of different dissociation constants on the equilibrium swelling ratio of the smart hydrogel. Recently, several macroscopic continuum theories were developed by considering the effect of different equilibrium constants on the responsive characteristic of different smart hydrogel (Chu *et al.*, 1995; De and Aluru, 2004; De *et al.*, 2002; Grimshaw *et al.*, 1990). In these models, the fixed charge density in the current state is influenced by the equilibrium constant. However, this section focuses on the analysis of the influence of the equilibrium constant on the ionic-strength-sensitive hydrogel.

In order to study the influence of different equilibrium constants on the equilibrium swelling/shrinking behavior of the hydrogel, the numerical simulation is conducted in this section by the MECis model with the following representative input data, the valence of fixed charge $z_f = -1$, the initial gel length $L_{gel}=2\text{mm}$, the computational domain length $L=10\text{mm}$, the initial mean distance between the fixed charges $r_0 = 60\text{nm}$, environmental solution temperature $T = 298$, the initial fixed

charge density $C_{s,0}^f = 300\text{mM}$, Young's modulus $E = 0.2\text{MPa}$, and the equilibrium constants $pK_0 = 2.8, 3.2, 3.6$ and 4.0 , respectively.

Figs. 3.15(c) and 3.16(c) show the distributions of the fixed charge densities C^f when the hydrogel reaches equilibrium state after it is placed in the solution with the ionic strengths of 3mM and 300mM for various equilibrium constants pK_0 . The fixed charges C^f distribute uniformly inside the hydrogel because of the isotropy and homogeneity of the hydrogel. As seen from the figures, the unbound fixed charge density C^f within the hydrogel after swelling increases with the increment of the equilibrium constant for both the bathing solution with ionic strengths of 3mM and 300mM . It is known from the MECis model that the fixed charge density C^f depends on several parameters, such as the ionic strength and the equilibrium constant pK_0 . For a given ionic strength, the increase of the equilibrium constant pK_0 leads to an increment of fixed charge density C^f . However, in the solution with the ionic strength of 300mM , the binding reaction between the mobile ions and fixed charge groups is much more active than that in the solution with 3mM for a given equilibrium constant. The fixed charge densities C^f for the ionic strength of 300mM are much smaller than those for the 3mM ionic strength.

The equilibrium concentration profiles of the positive ion C^+ and negative ion C^- for different equilibrium constants pK_0 are illustrated in Figs. 3.15(a)-(b) and 3.16(a)-(b) for the ionic strengths of 3mM and 300mM , respectively. The positive ions are attracted and bound on the hydrogel while the negative ions are repelled outside the hydrogel since the valence of the fixed charges is -1 . The concentration of the positive ion C^+ in the hydrogel is higher than that in the solution and rises with an increase in fixed charge density C^f , and decreases with an increase in the equilibrium constant pK_0 . On the other hand, the concentration of the negative ions C^- in the hydrogel is lower than that in the external solution, declining with an increase in the equilibrium constant pK_0 . In order to maintain the electroneutrality inside the hydrogel, the positive charges are attracted into the hydrogel and the negative charges are repelled out. The attraction and repulsion drive the positive and negative ions to diffuse into or out of the hydrogel, which produces the ionic concentration discrepancy

over the hydrogel-solution interface. The influence of the equilibrium constant pK_0 on the concentrations of the positive C^+ and negative ions C^- is mainly due to the binding reaction between the mobile ions and fixed charges, which leads to the different unbound fixed charge densities and then different ionic concentrations.

Figs. 3.15 (d) and 3.16(d) demonstrate the influence of different equilibrium constants pK_0 on the equilibrium electric potential ψ in both the hydrogel and surrounding solution with the ionic strengths of 3mM and 300mM, respectively. The electric potential ψ in the surrounding solution remains zero since the electroneutrality is satisfied. In the hydrogel however, the slightly different concentrations between the negative and positive charges lead to the electric potential. With the increase of the equilibrium constant pK_0 , the difference between the negative and positive charges also enlarges and thus the electric potential increases.

The equilibrium displacement profiles u of the hydrogel are shown in Figs. 3.15(e) and 3.16(e) for various equilibrium constants pK_0 of the hydrogel immersed in the solution with the ionic strengths of 3mM and 300mM, respectively. The figures illustrate how the hydrogel deforms as a function of the equilibrium constant pK_0 . Obviously, the hydrogel expands much more in the solution with low ionic strength (e.g., 3mM) than that with high ionic strength (e.g., 300mM), where the hydrogel in the solution with the ionic strength of 300mM almost keeps in compact state, and the displacement u is very small compared with the length of the hydrogel. However, in the solution with the ionic strength of 3mM, the deformation of the hydrogel is comparable to its length. This may be explained in the figures through the fixed charge density and the concentration of mobile ions. The bound reaction between the fixed charge groups and mobile ions drives the diffusion of the mobile ions into or out of the hydrogel, which produces the concentration difference over the hydrogel-solution interface. This difference leads to the osmotic pressure that makes the hydrogel swell. At lower ionic strength (e.g., 3mM), the ionic concentration difference over the hydrogel-solution interface becomes larger since more unbound fixed charges are left. As a result, the concentration difference of the mobile ions over the hydrogel-solution interface at low ionic strength is larger than that at high ionic strength, which drives the solid polymeric networks of the hydrogel to deform much more to balance the osmotic pressure. The influence of different equilibrium constants pK_0 on the

displacement is also reflected through the bound reaction. With a smaller value of pK_0 , the reaction is less active and therefore the osmotic pressure decreases, which causes the hydrogel to expand less.

The influence of various equilibrium constants pK_0 on the normalized equilibrium swelling ratio ESR is depicted in Fig. 3.14 for various ionic strengths. It is observed from the figure that, with the increase of the equilibrium constant pK_0 , the equilibrium swelling ratio ESR decreases when the hydrogel is immersed in the solution of low ionic strength (e.g., ranging from 10^{-4} to 0.05mM). However, the equilibrium swelling ratio ESR remains unchanged or changes slightly if the ionic strength is higher than 0.05mM. The bound reaction at low ionic strength is sensitive to the equilibrium constant. A small change of the equilibrium constant pK_0 may lead to a large change of the fixed charge density as shown in the figures, while the change of the mobile ions in the hydrogel is also considerable. Therefore, the osmotic pressure and repulsive force are influenced by different equilibrium constants, which affect the swelling ratio significantly. However, the bound reaction between the fixed charge groups and mobile ions is very active, and the fixed charge sites are almost fully occupied by the mobile ions when the hydrogel is immersed into the solution with high ionic strength. The variation of the equilibrium constant may slightly affect the fixed charges and the mobile ions, which also influences the swelling ratio faintly.

In conclusion, the equilibrium constant pK_0 and the ionic strength of the solution determine the activity of the bound reaction between the fixed charges and mobile ions. It is observed that, with an increase in the equilibrium constant pK_0 , the equilibrium swelling ratio ESR and fixed charge density C^f as well as the concentration of the positive ion C^+ decrease, but the concentration of the negative ions C^- and the electric potential ψ increase.

3.4.3. Influence of Young's Modulus

As the most important mechanical property of material, Young's modulus is widely used in evaluating the strength of hydrogels. In general, the Young's modulus of the hydrogel could be modified by changing the crosslinking time, using monomers with large modulus, or altering the amount of total monomer during synthesis (David *et al.*,

2004; Martens *et al.*, 2007; Matzelle *et al.*, 2003; Srivastava *et al.*, 2007). The elastic modulus of some hydrogels may also change with environmental conditions, such as temperature and concentration of surrounding solution (Wang *et al.*, 1997; Ye *et al.*, 2004). Most of the studies on the effect of Young's modulus on the swelling ratio were experiment-based (Baker *et al.*, 1994; Dhara *et al.*, 1999; Hooper *et al.*, 1990). Few of them were involved in theoretical modeling. In this section, the MECis model is employed for discussion of Young's modulus of the hydrogel, especially focusing on the effect of the variation of Young's modulus on the equilibrium distributions of mobile ions, fixed charge density, electric potential, displacement and swelling ratio.

The representative input data used in the parameter study are given as: the valence of the fixed charge $z_f = -1$, the initial length of gel domain $L_{gel}=4\text{mm}$, environmental temperature $T=298\text{K}$, the length of solution domain $L=10\text{mm}$, the initial charge distance $r_0 = 60\text{nm}$, intrinsic dissociation constant $pK_0 = 3.6$, and the initial fixed charge density $C_{s,0}^f = 800\text{mM}$. The three representative Young's moduli $E = 0.2, 0.4, 0.6\text{MPa}$ are discussed in details.

The dependence of the normalized equilibrium swelling ratio ESR on Young's modulus E is shown in Fig. 3.17. As observed from the figure, the Young's modulus E significantly influences the equilibrium swelling ratio ESR of the ionic-strength-sensitive hydrogel when immersed in the solution with low ionic strength, e.g., less than 10mM . However, the change of Young's modulus E has little effect on the equilibrium swelling ratio ESR of the hydrogel placed in a solution with high ionic strength, e.g., larger than 10mM . This interesting observation may result from the different states of the hydrogel when immersed in solution with different ionic strengths. For example, if the environmental ionic strength is low, the hydrogel swells greatly due to the osmotic pressure over the hydrogel-solution interface, and the increase of the Young's modulus may enhance the stiffness of the hydrogel, which reduces the deformation flexibility of the hydrogel. As a result, the swelling ratio drops with the increase of the Young's modulus of the hydrogel at a low ionic strength of surrounding solution. However, when the ionic strength of the solution is high, the hydrogel does not swell or swells trivially, such that the Young's modulus changes the state of the hydrogel insignificantly.

It is also seen from Fig. 3.17 that the normalized equilibrium swelling ratio ESR

decreases with the increase of Young's modulus E , and the interval between adjacent curves also decreases. This performance is observed more clearly in Fig. 3.18, where the swelling ratio decreases fast initially until Young's modulus is equal to about 0.6MPa, and then becomes slow. Fig. 3.18 also shows the different characteristics of the ionic-strength-sensitive hydrogel in the solution with low and high ionic strengths respectively, where the Young's modulus E influences the equilibrium swelling ratio ESR of the ionic-strength-sensitive hydrogel exponentially for low ionic strength, and almost linearly for high ionic strength.

Figs. 3.19(c) and 3.20(c) exemplify the equilibrium distributive profiles of the fixed charge density C^f within the hydrogel as a function of Young's modulus E , when the ionic strengths of solution are 1mM and 100mM, respectively. As observed from Fig. 3.19(c), the increase of Young's modulus E leads to the increment of the fixed charge density C^f and the shrinking of the hydrogel. The binding reaction between the fixed charges and mobile ions is influenced mainly by the deformation of the hydrogel, if Young's modulus E is changed. Therefore, the variation of the fixed charge density is almost controlled by the deformation of the hydrogel. From mathematical point of view, the fixed charge density C^f is the function of the initial fixed charge density $C_{s,0}^f$, the ionic strength I , the concentration of binding ions C_b , the intrinsic dissociation or binding constant K_0 , and the Jacobian of the hydrogel $\det \mathbf{F}$, as formulated in Eqn. (2.41). If $C_{s,0}^f$, I , K_0 and C_b are given, the Jacobian of the hydrogel $\det \mathbf{F}$ is what solely influences the fixed charge density. As Young's modulus E increases, the hydrogel shrinks and then the Jacobian $\det \mathbf{F}$ decreases, the fixed charge density thus increases. However, the influence of Young's modulus on the fixed charge density C^f is quite insignificant when the hydrogel is placed into a solution with the ionic strength of 100mM, as observed from Fig. 3.20(c), where the hydrogel almost remains in a compact state, and the variation of the swelling is insignificant with Young's modulus. The fixed charge density C^f thus changes slightly.

The equilibrium distributive patterns of the positive ionic concentration C^+ are almost similar to that of the fixed charge density, as observed in Figs. 3.19(a) and 3.20(a). The fixed charges with the valence of -1 attract the positive ions into the

hydrogel and repel the negative ions out of the hydrogel to maintain the electroneutrality inside the hydrogel. Therefore, the concentration of the positive ions C^+ increases with the fixed charge density C^f in the interior hydrogel, and keeps constant in the external solution. In contrast, the concentration of the negative ions C^- decreases with the increase of the Young's modulus as known from Fig. 3.19(b) for the ionic strength of 1mM. However, the distributions of the positive C^+ and negative ions C^- in the solution with the ionic strength of 100mM also change slightly, as observed from Figs. 3.20(a) and (b).

The equilibrium profiles of the electric potential ψ distributed in the hydrogel and solution are illustrated in Figs. 3.19(d) and 3.20(d). The electric potential ψ is associated with the concentration of the mobile ions and/or fixed charges, as formulated in the MECis model. In the environmental solution, the electric potential ψ remains constant since the electroneutrality condition is already satisfied. In the hydrogel however, there is a small difference between the concentrations of the positive C^+ and negative C^- ions, which produces the nonzero electric potential ψ . With an increase in the Young's modulus E , the difference increases and thus it enlarges the electric potential.

The equilibrium displacement profiles u of the hydrogel are illustrated in Figs. 3.19(e) and 3.20(e). It can be observed that the effect of the Young's modulus E on the displacement u seems to be due directly to the apparent relation between the displacement and the Young's modulus in the mechanical field. The displacement u of the hydrogel is changed largely with the variation of the Young's modulus E , when the hydrogel is immersed into the lower ionic-strength solution. The large Young's modulus strengthens the hydrogel and makes the polymeric network more compact. Since the osmotic pressure and repulsive force as driving source are equilibrated by the network strength, increasing the Young's modulus E could equilibrate a larger driving force. As such, the strain of the hydrogel becomes smaller when increasing the Young's modulus, which obviously leads to the small displacement.

In summary, Young's modulus E has a nonlinear effect on the equilibrium swelling ratio ESR of the ionic-strength-sensitive hydrogel. With the increase of the Young's modulus E , the equilibrium swelling ratio ESR and concentration of the

negative ions C^- as well as electric potential ψ decrease, although the fixed charge density C^f and positive ionic concentration C^+ increase.

3.4.4. Influence of Initial Distance between Fixed Charges

The initial distance between the fixed charges, or briefly called the initial charge distance, is a significant material parameter at microscopic level, since the chemical-expansion stress is due to the charge-to-charge electrostatic repulsive force (Lai *et al.*, 1991). In this section, the influence of the initial charge distance on the swelling/shrinking of the ionic-strength-sensitive hydrogel is analyzed in a detailed discussion.

For analysis of the initial charge distance by the present MECis model, the representative input data are given as: the gel domain length $L_{gel} = 2\text{mm}$, the whole computational domain length including the gel and solution lengths $L = 10\text{mm}$, the valence of the fixed charge $z_f = -1$, Young's modulus $E = 0.4\text{MPa}$, the initial fixed charge density $C_0^f = 800\text{mM}$, the intrinsic dissociation constant $K_0 = 10^{-3.6}$, and the temperature $T = 298\text{K}$. The initial charge distances are given as $r_0 = 8, 10, 12\text{nm}$ in simulation for parameter studies. The analysis of the effect of the initial charge distance on the characteristics of the ionic-strength-sensitive hydrogel is carried out for two different ionic strengths, 1mM and 100mM, as the examples of the low and high ionic strengths, respectively.

In terms of the variation of the equilibrium swelling ratio ESR with the initial charge distance r_0 , Fig. 3.21 depicts the normalized equilibrium swelling ratio ESR as a function of the ionic strength when the initial charge distance r_0 changes, and Fig. 3.22 gives the equilibrium swelling ratio ESR as a function of the initial charge distance r_0 when the ionic strengths of the surrounding solution are taken as 1mM and 100mM respectively. It is observed from Fig. 3.21 that the increase of the initial charge distance r_0 reduces the equilibrium swelling ratio ESR of the hydrogel. This is because the increase of the initial charge distance r_0 decreases the electrostatic force between two charges and thus the expansion force decreases. It is demonstrated in Fig. 3.22 that the deswelling behavior with the increase of the initial

charge distance r_0 follows an exponential pattern nonlinearly at low ionic strength such as 1mM. This nonlinearity could be understood from the Debye shielding effect. The Debye length is a screening length, over which the effect of the point charge is negligible to the other charges. When the initial charge distance is less than the Debye length $r_0 < \kappa$, there exists the electrostatic force between the fixed charges, and the increase of the initial charge distance has the negligible effect on the swelling ratio. However, when the initial charge distance is larger than the Debye length $r_0 > \kappa$, e.g. 15nm in the present case study, the effect of the electrostatic force between the fixed charges is screened and thus the repulsive force influences the equilibrium swelling of the hydrogel slightly. Therefore, the increase of the initial charge distance no longer influences the equilibrium swelling ratio ESR . It is known that the Debye length is associated with the ionic strength of the interstitial solution. The ionic strength has a reciprocal effect on the Debye length. Therefore, at high ionic strength such as 100mM, the Debye length may become much small, e.g. less than 8nm in the present case study. The effect of the initial charge distance on the equilibrium swelling ratio ESR is thus negligible.

Figs. 3.23(c) and 3.24(c) describe the equilibrium distributive profiles of the fixed charge density C^f for the ionic strength of 1mM and 100mM in the hydrogel and solution regions. The interface between the hydrogel and solution is smoothed for better computation, and moves from left to right as the hydrogel swells. It is shown that the increase in initial charge distance r_0 leads to an increase in the fixed charge density C^f . As discussed above, the increase of the initial charge distance r_0 decreases the equilibrium swelling ratio ESR . For given all other parameters, if the equilibrium swelling ratio ESR increases, the volume of the hydrogel also increases, which decreases the fixed charge density C^f . However, when the ionic strength is high such as 100mM, the initial charge distance r_0 has very slight influence on the fixed charge density C^f . As shown in the figures, the fixed charge density C^f reflects the activity of the interaction between the polymer and mobile ions. As observed from the figures, when the ionic strength is low such as 1mM, the fixed charge density is larger than 7mM, while it is less than 3mM for the ionic strength of 100mM. It is thus concluded that the more fixed charge sites are bound at the higher

ionic strength.

Figs. 3.23(a) and 3.24(a) illustrate the equilibrium distributions of the concentration of positive ions C^+ , in which the variation of the concentration with the initial charge distance r_0 has the similar pattern to that with the fixed charge density C^f . Since the valence of the fixed charge density z_f is -1 , the positive ions are attracted into the hydrogel to maintain the electroneutrality. With the increase of the initial charge distance r_0 , the unbound fixed charge density increases and more positive ions are attracted for the electroneutrality inside the hydrogel. As a result, the concentration of the positive ions C^+ also increases. The electroneutrality condition inside the hydrogel also repels the negative ions out of the hydrogel, as illustrated in Figs. 3.23(b) and 3.24(b). These figures provide the equilibrium distribution of concentration of the negative ions C^- in both the hydrogel and solution regions at the ionic strengths of 1mM and 100mM. The concentration of the negative ions C^- decreases with the increase of the initial charge distance r_0 . The electroneutrality can be proved by summation of all the concentrations of the fixed charges C^f and the positive ions C^+ as well as the negative ions C^- together with the corresponding valences, where the result is almost equal to zero.

The small variation of the summation of the concentrations of the positive and negative charges around zero produces the electric potential ψ along the hydrogel and solution region, as illustrated in Figs. 3.23(d) and 3.24(d). It is seen from the figures that the increase of the initial charge distance r_0 causes the decrease of the electric potential ψ . Probably, the main contribution of electric potential ψ in the hydrogel comes from the negative ions. It is also observed that the electric potential ψ at low ionic strength such as 1mM is less than that at high ionic strength such as 100mM. That is because the initial charge distance at low ionic strength has much more influence on the electroneutrality inside the hydrogel.

Figs. 3.23(e) and 3.24(e) show that the equilibrium displacement u profile of the hydrogel with different initial charge distances for low and high ionic strengths. They give a deeper insight into the deformation of the hydrogel. The initial charge distance r_0 influences the displacement u obviously, by the apparent relation between the

displacement and the initial charge distance in the mechanical field. The displacement of the hydrogel u is changed largely with the variation of the initial charge distance r_0 when the hydrogel is immersed into the low ionic strength solution, while it is changed slightly in the solution of high ionic strength.

In brief, the charge distance r_0 affects the characteristics of ionic-strength-sensitive hydrogels through the electrostatic repulsive force among the fixed charges. The influence of charge distance r_0 on the equilibrium swelling ratio reflects the Debye shielding effect at micro-level. It is observed that, with the increase of charge distance r_0 , the fixed charge density C^f and concentration of positive ionic C^+ increase, while the concentration of the negative ions C^- as well as electric potential ψ decrease.

3.5. Summary

In this chapter, the equilibrium analysis of the ionic-strength-sensitive hydrogel is conducted using the steady-state MECis model. It is shown that the smart hydrogel shrinks when increasing the ionic strength of the solution. The mechanism is explained by the MECis model as follows.

- When the ionic strength of surrounding solution is low, the hydrogel dissociates in an attempt to maintain the equilibrium of dissociation and binding. As a result, the hydrogel obtains greater fixed charge density, which requires a larger number of mobile counterions diffusing into the interior hydrogel, and repels the mobile ions with charge of the same sign as the fixed charge, in order to maintain the electroneutrality within the hydrogel.
- The concentration difference between the interior hydrogel and exterior solution increases tremendously, leading to higher osmotic pressure which creates higher degree of swelling/shrinking.
- Meanwhile, the elastic retractive force of the polymer network is developed to expand network.
- With the increase of the ionic strength, more mobile ions are bound to the fixed charge sites and less fixed charges are left, which require less mobile ions to diffuse in and out of the hydrogel. The concentration difference and the osmotic pressure thus lower.

- As a consequence, the hydrogel shrinks. Meanwhile, the increase of the ionic strength also reduces the Debye length and the effect of repulsive force on the swelling.

The MECis model is compared with experiments for the PAAP, PAI, PAAS and PAMC hydrogels which are responsive to environmental ionic strength (Caykara and Dogmus, 2005; Dhara *et al.*, 1999; Hooper *et al.*, 1990; Okay *et al.*, 1998), in order to validate the MECis model. They represent different properties of the ionic-strength-sensitive hydrogel. For example, they dissociate either weakly (PAAP, PAI) or strongly (PAAS, PAMC) in solution. Their dimensions vary from 4 to 18 mm. The initial fixed charge density also changes from low (47mM) to high (3459mM). In addition, their strengths cover different ranges. The comparisons shows that the simulation results by the MECis model for the equilibrium swelling ratio of the ionic-strength-sensitive hydrogel are in good agreement with the experimental data (Caykara and Dogmus, 2005; Dhara *et al.*, 1999; Hooper *et al.*, 1990; Okay *et al.*, 1998). It is therefore concluded that the MECis model is able to efficiently predict the swelling/shrinking behavior of the different ionic-strength-sensitive hydrogels quantitatively and qualitatively.

The MECis model is then compared with three theories, namely the modified Flory-Rehner theory-I and II, and the gel-swelling model, where mixing and elastic contributions are derived from the lattice model, while the ionic contribution results from the ideal Donnan equilibrium. However, it is noted that there are several drawbacks in the Flory-Rehner and gel-swelling theories. For instance, the lattice model only concerns the behavior of microscopic molecules but does not include the macroscopic properties of the materials. The ideal Donnan equilibrium is suitable for dilute solution, and is not strictly proven for the concentrated solution. Further, the electric field induced from the fixed charges and mobile ions is not included in the theory. These drawbacks restrict the applicability of the Flory-Rehner theory to wider areas. However, the MECis model includes the macroscopic behavior of the hydrogel, and also considers the microscopic force between the fixed charges. The interactions of the mobile-mobile ions and mobile-ions-fixed-charges make the main contribution to the deformation of the hydrogel. In the MECis model, no assumption of the electroneutrality is made within the hydrogel. Alternatively, an electric potential exists in the hydrogel, which makes the MECis model more realistic. Furthermore, the MECis model covers two regions including the hydrogel and external solution

multiple domains, such that it is able to analyze the characteristics of both the hydrogel and external solution.

In addition, the parameter studies give an insight into the characteristics of the ionic-strength-sensitive hydrogel, subjected to the effects of initial fixed charge density, the equilibrium constant, Young's modulus, and initial fixed charge distance. These parameters can be determined or changed when synthesizing the hydrogel, and they cannot be neglected for both the application and theoretical development of the hydrogels. The distributions of several important field variables, including the fixed charge density, the mobile ions including positive and negative ions, the electric potential and the displacement, are extracted by the MECis model and analyzed in detail. It is summarized that the ionic-strength-sensitive hydrogel has different characteristics when immersed into solutions with low and high ionic strengths. Therefore, the influence of the parameters on the swelling ratio, ionic concentrations and electric potential has to be investigated in two phases, at low and high ionic strengths respectively.

In conclusion, the present MECis theory is capable of modeling the equilibrium characteristics of the ionic-strength-sensitive hydrogel, and analyzing the influence of various physical and chemical parameters, including the initial fixed charge density, the equilibrium constant, Young's modulus, and the initial fixed charge distance,. The MECis model is also capable of providing the complete picture of both the hydrogel and solution, such as the distributions of the ionic species, fixed charge density, electric potential and deformation. These critical findings will be useful in the design and optimization of hydrogel-based BioMEMS devices.

Table 3.1. Physical and chemical parameters of PAAP hydrogel.

Parameters	Value
Environmental ionic strength $I(\text{M})$ (Dhara <i>et al.</i> , 1999)	$10^{-4} \sim 3$
Initial diameter of hydrogel (mm) (Dhara <i>et al.</i> , 1999)	18
Initial fixed charge density $C_0^f(\text{mM})$	881.7(A1), 1753.7(A2), 2600.6(A3), 3428.4 (A4)
Initial fixed charge distance $r_0(\text{nm})$ (Shukla and Bajpai, 2006)	$8.2 \sim 73.1$
Intrinsic dissociation constant $pK_0(\text{M})$ (Burke and Barrett, 2003; Vink, 1986)	3.6
Temperature $T(\text{K})$ (Dhara <i>et al.</i> , 1999)	298
Valence of fixed charge z_f (Dhara <i>et al.</i> , 1999)	-1
Young's modulus $E(\text{MPa})$ (Lopez-Ureta <i>et al.</i> , 2008; Martens <i>et al.</i> , 2007)	$0.013 \sim 1$

Table 3.2. Physical and chemical parameters of PAI hydrogel.

Parameters	Value
Environmental ionic strength $I(\text{M})$ (Caykara and Dogmus, 2005)	$10^{-4} \sim 1$
Initial diameter of hydrogel (mm) (Caykara and Dogmus, 2005)	4
Initial fixed charge density(mM) (Caykara and Dogmus, 2005; Caykara <i>et al.</i> , 2004)	943(PAI-1), 2075.6(PAI-2), 3459(PAI-3)
Initial fixed charge distance $r_0(\text{nm})$	30.7, 17.8, 15.6
Intrinsic dissociation constant $pK_0(\text{M})$ (Kortum <i>et al.</i> , 2000; Uyanik and Erbil, 2000)	3.85
Temperature $T(\text{K})$ (Caykara and Dogmus, 2005)	298
Valence of fixed charge z_f (Caykara and Dogmus, 2005)	-1
Young's modulus $E(\text{kPa})$ (Matzelle <i>et al.</i> , 2003; Vallés <i>et al.</i> , 2000)	8 ~ 350

Table 3.3. Physical and chemical parameters of PAAS hydrogel.

Parameters	Value
Environmental ionic strength $I(\text{M})$ (Okay <i>et al.</i> , 1998)	$10^{-4} \sim 1$
Initial diameter of hydrogel (mm) (Okay <i>et al.</i> , 1998)	5.8
Initial fixed charge density (mM)	0, 47, 94, 140, 276
Initial fixed charge distance $r_0(\text{nm})$ (Kizilay and Okay, 2003; Russell and Carta, 2005)	25
Intrinsic binding constant $K_0(\text{M}^{-1})$ (Kasseh and Keh, 2006)	10^4
Temperature $T(\text{K})$ (Okay <i>et al.</i> , 1998)	294
Valence of fixed charge z_f (Okay <i>et al.</i> , 1998)	-1
Young's modulus $E(\text{MPa})$ (Matzelle <i>et al.</i> , 2003)	0.165

Table 3.4. Physical and chemical parameters of T-series of PAMC hydrogel.

Parameters	Value
Environmental ionic strength $I(\text{M})$ (Hooper <i>et al.</i> , 1990)	$10^{-4} \sim 1$
Initial diameter of hydrogel (mm) (Hooper <i>et al.</i> , 1990)	10
Initial fixed charge density (mM)	343, 457, 572
Initial fixed charge distance $r_0(\text{nm})$ (Kizilay and Okay, 2003; Russell and Carta, 2005)	25
Intrinsic binding constant $K_0(\text{M}^{-1})$ (Miura <i>et al.</i> , 1999)	$10^{3.8}$
Temperature $T(\text{K})$ (Hooper <i>et al.</i> , 1990)	298
Valence of fixed charge z_f (Hooper <i>et al.</i> , 1990)	+1
Young's modulus $E(\text{MPa})$ (Matzelle <i>et al.</i> , 2003)	$0.1 \sim 0.35$

Table 3.5. Physical and chemical parameters of C-series of PAMC hydrogel.

Parameters	Value
Environmental ionic strength $I(\text{M})$ (Hooper <i>et al.</i> , 1990)	$10^{-4} \sim 1$
Initial diameter of hydrogel (mm) (Hooper <i>et al.</i> , 1990)	10
Initial fixed charge density (mM)	343, 343, 343, 340, 325
Initial fixed charge distance $r_0(\text{nm})$ (Kizilay and Okay, 2003; Russell and Carta, 2005)	25
Intrinsic binding constant $K_0(\text{M}^{-1})$ (Miura <i>et al.</i> , 1999)	$10^{3.8}$
Temperature $T(\text{K})$ (Hooper <i>et al.</i> , 1990)	298
Valence of fixed charge z_f (Hooper <i>et al.</i> , 1990)	+1
Young's modulus $E(\text{MPa})$ (Matzelle <i>et al.</i> , 2003)	$0.1 \sim 0.35$

Table 3.6. Physical and chemical parameters of M-series of PAMC hydrogel.

Parameters	Value
Environmental ionic strength $I(\text{M})$ (Hooper <i>et al.</i> , 1990)	$10^{-4} \sim 1$
Initial diameter of hydrogel (mm) (Hooper <i>et al.</i> , 1990)	10
Initial fixed charge density (mM)	0, 175, 343, 504, 660, 810
Initial fixed charge distance $r_0(\text{nm})$ (Kizilay and Okay, 2003; Russell and Carta, 2005)	25
Intrinsic binding constant $K_0(\text{M}^{-1})$ (Miura <i>et al.</i> , 1999)	$10^{3.8}$
Temperature $T(\text{K})$ (Hooper <i>et al.</i> , 1990)	298
Valence of fixed charge z_f (Hooper <i>et al.</i> , 1990)	+1
Young's modulus $E(\text{MPa})$ (Matzelle <i>et al.</i> , 2003)	$0.1 \sim 0.35$

Fig. 3.1. Computational domain and boundary conditions for the one-dimensional simulation.

Fig. 3.2. Equilibrium swelling ratios of the MECis model and experimental data (Dhara *et al.*, 1999) for the A1 series of PAAP hydrogels.

Fig. 3.3. Equilibrium swelling ratios of the MECis model and experimental data (Dhara *et al.*, 1999) for the A2 series of PAAP hydrogels.

Fig. 3.4. Equilibrium swelling ratios of the MECis model and experimental data (Dhara *et al.*, 1999) for the A3 series of PAAP hydrogels.

Fig. 3.5. Equilibrium swelling ratios of the MECis model and experimental data (Dhara *et al.*, 1999) for the A4 series of PAAP hydrogels.

Fig. 3.6. Equilibrium swelling ratios of the MECis model and experimental data (Caykara and Dogmus, 2005) for PAI hydrogel.

Fig. 3.7. Equilibrium swelling ratios of the MECis model, Flory-Rehner theory and experimental data (Okay *et al.*, 1998) for PAAS hydrogel.

Fig. 3.8. Equilibrium swelling ratios of the MECis model, gel-swelling model, and experimental data (Hooper *et al.*, 1990) for the T-series of PAMC hydrogels.

Fig. 3.9. Equilibrium swelling ratios of the MECis model, gel-swelling model, and experimental data (Hooper *et al.*, 1990) for the C-series of PAMC hydrogels.

Fig. 3.10. Equilibrium swelling ratios of the MECis model, gel-swelling model, and experimental data (Hooper *et al.*, 1990) for the M-series of PAMC hydrogels.

Fig. 3.11. Influence of the initial fixed charge density C_0^f on the normalized equilibrium swelling ratio ESR for the ionic-strength sensitive hydrogel.

Fig. 3.12. Influence of the initial fixed charge density C_0^f on the equilibrium distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution with the ionic strength of 1mM.

Fig. 3.13. Influence of the initial fixed charge density C_0^f on the equilibrium distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution with the ionic strength of 100mM.

Fig. 3.14. Influence of the equilibrium constant pK_0 on the normalized equilibrium swelling ratio ESR for the ionic-strength sensitive hydrogel.

Fig. 3.15. Influence of the equilibrium constant pK_0 on the equilibrium distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution with the ionic strength of 3mM.

Fig. 3.16. Influence of the equilibrium constant pK_0 on the equilibrium distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution with the ionic strength of 300mM.

Fig. 3.17. Influence of Young's modulus E on the normalized equilibrium swelling ratio ESR for the ionic-strength sensitive hydrogel.

Fig. 3.18. Influence of the Young's modulus E on the swelling behavior of the ionic-strength-sensitive hydrogel immersed in the solution with the ionic strength of 1mM and 100mM.

Fig. 3.19. Influence of the Young's modulus E on the equilibrium distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution with the ionic strength of 1mM.

Fig. 3.20. Influence of the Young's modulus E on the equilibrium distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution with the ionic strength of 100mM.

Fig. 3.21. Influence of the initial fixed charge distance r_0 on the normalized equilibrium swelling ratio ESR for the ionic-strength-sensitive hydrogel.

Fig. 3.22. Influence of the initial fixed charge distance r_0 on the swelling behavior of the ionic-strength-sensitive hydrogel immersed in the solution with the ionic strength of 1mM and 100mM.

Fig. 3.23. Influence of the initial fixed charge distance r_0 on the equilibrium distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution with the ionic strength of 1 mM.

Fig. 3.24. Influence of the initial fixed charge distance r_0 on the equilibrium distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution with the ionic strength of 100mM.

4

Kinetic Analysis of Ionic-Strength-Sensitive Hydrogel

4.1. Introduction

The kinetics of smart hydrogels have recently attracted the attention of researchers worldwide, as proposed applications of the smart hydrogel require further understanding of kinetic swelling/shrinking, such as drug delivery (Bawa *et al.*, 2009; Hamidi *et al.*, 2008; Kim *et al.*, 1992) and other biomedical applications (Alarcon *et al.*, 2005; Hoffman, 2002). So far, numerous studies of the kinetic phenomena have been carried out experimentally and theoretically (Bajpai, 2001; Chen *et al.*, 2005; Coviello *et al.*, 1999; Goel *et al.*, 2006a; Jeon *et al.*, 1998; Li *et al.*, 2006a; Lin *et al.*, 2009).

In this chapter however, the analysis of the kinetic swelling/shrinking of the ionic-strength-sensitive hydrogels is carried out using the present MECis model, via a series of parametric studies. The objective of the present investigation is not only to demonstrate the capability of the MECis model for simulation of the kinetic characteristics of the ionic-strength-sensitive hydrogel, but also to perform the parametric studies of several important physical and chemical properties of the hydrogel and solution.

Firstly, the numerical techniques are introduced. These include the nondimensionalization strategy, the discretization of both the temporal and spatial domains by the Hemite-cloud (Li *et al.*, 2003) and the Newmark methods, and the transient algorithm, in order to numerically analyze the kinetics of the ionic-strength-sensitive hydrogels by the MECis model. Apart from those, the initial and boundary conditions for the problems are also specified. In addition, an obstruct model (De *et al.*, 2002) is applied to modify the diffusion coefficient of the mobile ions inside the hydrogel.

In order to examine the computational robust and accuracy of the transient MECis model, the simulations are compared with published experiments for the kinetic swelling/shrinking of ionic-strength-sensitive hydrogels, where four types of the hydrogels are investigated, covering the kinetics of different physical and chemical characteristics of ionic-strength-sensitive hydrogels.

In addition, the kinetic parameter studies of the ionic-strength-sensitive hydrogel are carried out with the MECis model. The reversible kinetics and influences of the initial fixed charge density and Young's modulus on kinetic swelling of hydrogels are analyzed, where the kinetic behaviors of chemical, electrical and mechanical variables are studied in detail, which include the ionic concentration, the fixed charge density, the electric potential, and the displacement.

4.2. Numerical Technique

4.2.1. Nondimensional Implementation

The same nondimensionalisation procedure used in Chapter 3, as shown in Eqn. (3.1), is also applied here. In addition, the diffusion coefficient D^a is nondimensionalized as

$$\bar{D}^a = \frac{D^a \delta t}{L_{ref}^2} \quad (4.1)$$

where δt is the reference time, and $\bar{D}^a$ is the nondimensional diffusion coefficient of the a th ionic species.

After nondimensionalization of Eqs. (2.60), (2.61), (2.62) and (2.67), the transient governing and constitutive equations are expressed as

$$\frac{\partial \bar{C}^a}{\partial t} = \frac{\bar{D}^a}{\delta t \lambda_1^2} \left[\bar{\beta}^a(\bar{I}) \left(\frac{\bar{C}^a \partial^2 \bar{I}}{\partial \bar{X}^2} + \frac{\partial \bar{C}^a}{\partial \bar{X}} \frac{\partial \bar{I}}{\partial \bar{X}} \right) + \frac{\partial^2 \bar{C}^a}{\partial \bar{X}^2} + z_a \theta \left(\frac{\bar{C}^a \partial^2 \bar{\psi}}{\partial \bar{X}^2} + \frac{\partial \bar{C}^a}{\partial \bar{X}} \frac{\partial \bar{\psi}}{\partial \bar{X}} \right) \right] \quad (4.2)$$

$$\frac{\varepsilon}{\lambda_1} \frac{\partial^2 \bar{\psi}(X, t)}{\partial \bar{X}^2} + \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} \left(z_f \bar{C}^f(X, t) + \sum_b z_b \bar{C}^b(X, t) \right) = 0 \quad (4.3)$$

$$\bar{C}^f(X, t) = \frac{\phi_0^s \bar{C}_{s,0}^f \bar{K}_0 \exp \left[\bar{\alpha}_1 \ln(10) (2|z^b| - 1) \sqrt{\bar{I}} / (1 + \bar{\alpha}_2 \sqrt{\bar{I}}) \right]}{\bar{K}_0 \exp \left[\bar{\alpha}_1 \ln(10) (2|z^b| - 1) \sqrt{\bar{I}} / (1 + \bar{\alpha}_2 \sqrt{\bar{I}}) \right] + \bar{C}^b(X, t)} \quad (4.4)$$

$$\begin{aligned}
 (l + 2m) & \left[\frac{d^2 \bar{u}(X, t)}{d\bar{X}^2} + 3 \frac{d\bar{u}(X, t)}{d\bar{X}} \frac{d^2 \bar{u}(X, t)}{d\bar{X}^2} + \frac{3}{2} \left(\frac{d\bar{u}(X, t)}{d\bar{X}} \right)^2 \frac{d^2 \bar{u}(X, t)}{d\bar{X}^2} \right] \\
 & + \frac{c_{ref} q F \bar{C}^f(X, t)}{8\pi \epsilon \kappa} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \left(\frac{\partial^2 \bar{u}}{\partial \bar{X}^2} \right) \\
 & - \frac{c_{ref} q F}{8\pi \epsilon r} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \frac{\partial \bar{C}^f(X, t)}{\partial \bar{X}} - \frac{c_{ref} R T}{\lambda_1} \sum_a \frac{\partial \bar{C}^a(X, t)}{\partial \bar{X}} = 0
 \end{aligned} \tag{4.5}$$

It is noted here that the generation rate in chemical field and the body force in mechanical field are neglected. In addition, all the above field variables are time dependent, thus Eqn. (4.2) is dynamic and Eqs. (4.3) to (4.5) are actually *quasi-static* equations.

4.2.2. Initial Condition

The computational domain is the same as that in Chapter 3, as shown in Fig. 3.1, based on the similar simplification conditions stated in Subsection 3.2.2. The boundary conditions are also imposed in a similar way as Eqn. (3.8).

In this chapter, the kinetics of hydrogel swelling or shrinking from one equilibrium state to another by changing the ionic strength of the solution is investigated. The initial equilibrium state is such that the ionic concentrations, the fixed charge density, the electric potential, and the deformation are all in equilibrium under a given ionic strength condition. The initial conditions are therefore imposed on the basis of the equilibrium state simulated by the steady-state MECis model, and they may be expressed as

$$\begin{aligned}
 \bar{C}^a(\bar{X}, 0) &= \bar{C}_0^a(\bar{X}), \quad \bar{C}^f(\bar{X}, 0) = \bar{C}_{s,0}^f(\bar{X}) \\
 \bar{\psi}(\bar{X}, 0) &= \bar{\psi}_0(\bar{X}), \quad \bar{u}(\bar{X}, 0) = \bar{u}_0(\bar{X})
 \end{aligned} \tag{4.6}$$

where $\bar{C}_0^a(\bar{X})$, $\bar{C}_{s,0}^f(\bar{X})$, $\bar{\psi}_0(\bar{X})$ and $\bar{u}_0(\bar{X})$ are the initial profiles of the mobile ionic concentration, fixed charge density, electric potential and displacement, respectively. As shown in Fig. 4.1 for the initial equilibrium, in the external solution, the fixed charge density and the electric potential are zero and the concentrations of mobile ions are based on the applied ionic strength; in the hydrogel however, the concentrations of the mobile ions, the fixed charge density, the electric potential and the displacement are obtained from the simulation of the steady-state MECis model. It is noted in Fig. 4.1 that the ionic concentrations, the electric potential, and the fixed

charge density have a step change over the hydrogel-solution interface at the initial equilibrium state.

4.2.3. Temporal and Spatial Discretizations

There are basically two methods for temporal discretization, namely the explicit and implicit methods. The explicit method requires the time interval less than a critical value to achieve numerical stability, and is dependent on the specified problems. However, the time interval of the implicit method is much larger than that of the explicit method in general, and is even unconditionally stable for some cases (Belytschko *et al.*, 2001). In this chapter, the Newmark method is applied for temporal discretization (Belytschko *et al.*, 2001)

$$\begin{aligned}\frac{\partial \bar{C}^a}{\partial t} \Big|^{t+\gamma\Delta t} &= \frac{\bar{C}^{a(t+\Delta t)} - \bar{C}^{a(t)}}{\Delta t} \\ \frac{\partial \bar{C}^a}{\partial t} \Big|^{t+\gamma\Delta t} &= (1-\gamma) \frac{\partial \bar{C}^a}{\partial t} \Big|^t + \gamma \frac{\partial \bar{C}^a}{\partial t} \Big|^{t+\Delta t} \\ \bar{C}^{a(t+\Delta t)} - \Delta t \gamma \frac{\partial \bar{C}^a}{\partial t} \Big|^{t+\Delta t} &= \bar{C}^{a(t)} + \Delta t (1-\gamma) \frac{\partial \bar{C}^a}{\partial t} \Big|^t\end{aligned}\tag{4.7}$$

where $\bar{C}^{a(t+\Delta t)}$ and $\bar{C}^{a(t)}$ are the concentrations of the a th ionic species at time $t + \Delta t$ and t , respectively. $0 \leq \gamma \leq 1$ is a weight coefficient to control the time integration. If $\gamma = 0$, it is an explicit method; if $\gamma = 1$, it becomes an implicit method. In order to achieve better stability, γ should be larger than 0.5 (i.e., $\gamma > 0.5$). By Eqn. (4.2), the time derivative at time t is therefore given as,

$$\begin{aligned}\frac{\partial \bar{C}^a}{\partial t} \Big|^t &= \frac{\bar{D}^{a(t)}}{\Delta t \lambda_1^2} \left[\bar{\beta}^{a(t)}(\bar{I}) \left(\frac{\bar{C}^{a(t)} \partial^2 \bar{I}^t}{\partial \bar{X}^2} + \frac{\partial \bar{C}^{a(t)}}{\partial \bar{X}} \frac{\partial \bar{I}^t}{\partial \bar{X}} \right) \right] \\ &+ \frac{\bar{D}^{a(t)}}{\Delta t \lambda_1^2} \left[\frac{\partial^2 \bar{C}^{a(t)}}{\partial \bar{X}^2} + z_a \theta \left(\frac{\bar{C}^{a(t)} \partial^2 \bar{\psi}^t}{\partial \bar{X}^2} + \frac{\partial \bar{C}^{a(t)}}{\partial \bar{X}} \frac{\partial \bar{\psi}^t}{\partial \bar{X}} \right) \right]\end{aligned}\tag{4.8}$$

From the above temporal discretization (4.8) with Hermite-cloud method spatial discretization (Li *et al.*, 2003), the discretization of the governing and constitutive equations (4.2)-(4.5) is given as

$$\begin{aligned}
 & \bar{C}^{a(t+\Delta t)} - \\
 & \frac{\gamma \bar{D}^{a(t+\Delta t)} \bar{\beta}^{a(t+\Delta t)}}{\lambda_1^2} \left[N_n(\bar{X}_i) \bar{C}_n^{a(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t+\Delta t)} \right] \\
 & \times \left[\frac{1}{2} \sum_b z_b^2 N_{n,XX}(\bar{X}_i) \bar{C}_n^{b(t+\Delta t)} \right] \\
 & + \frac{\gamma \bar{D}^{a(t+\Delta t)}}{\lambda_1^2} \bar{\beta}^{a(t+\Delta t)}(\bar{I}) \left[M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t+\Delta t)} \right] \left[\frac{1}{2} \sum_b z_b^2 M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} \right] \\
 & + \frac{\gamma \bar{D}^{a(t+\Delta t)}}{\lambda_1^2} N_{n,XX}(\bar{X}_i) \bar{C}_n^{a(t+\Delta t)} \\
 & + \frac{z_a \theta \gamma \bar{D}^{a(t+\Delta t)}}{\lambda_1^2} \left[N_n(\bar{X}_i) \bar{C}_n^{a(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t+\Delta t)} \right] \\
 & \times \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n^{(t+\Delta t)} \right] \\
 & + \frac{z_a \theta \gamma \bar{D}^{a(t+\Delta t)}}{\lambda_1^2} \left[M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t+\Delta t)} \right] \left[M_m(\bar{X}_i) \bar{\psi}_{m,X}^{(t+\Delta t)} \right] \tag{4.9}
 \end{aligned}$$

$$\begin{aligned}
 & = \\
 & \bar{C}^{a(t)} - \frac{\gamma \bar{D}^{a(t)} \bar{\beta}^{a(t)}}{\lambda_1^2} \left[N_n(\bar{X}_i) \bar{C}_n^{a(t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t)} \right] \times \\
 & \left[\frac{1}{2} \sum_b z_b^2 N_{n,XX}(\bar{X}_i) \bar{C}_n^{b(t)} \right] \\
 & + \frac{\gamma \bar{D}^{a(t)}}{\lambda_1^2} \bar{\beta}^{a(t)}(\bar{I}) \left[M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t)} \right] \left[\frac{1}{2} \sum_b z_b^2 M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t)} \right] \\
 & + \frac{\gamma \bar{D}^{a(t)}}{\lambda_1^2} N_{n,XX}(\bar{X}_i) \bar{C}_n^{a(t)} \\
 & + \frac{z_a \theta \gamma \bar{D}^{a(t)}}{\lambda_1^2} \left[N_n(\bar{X}_i) \bar{C}_n^{a(t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t)} \right] \\
 & \times \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n^{(t)} \right] + \frac{z_a \theta \gamma \bar{D}^{a(t)}}{\lambda_1^2} \left[M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t)} \right] \left[M_m(\bar{X}_i) \bar{\psi}_{m,X}^{(t)} \right] \\
 & \frac{\varepsilon}{\lambda_1} \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n^{(t+\Delta t)} \right] + \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} z_f \bar{C}^{f(t+\Delta t)}(X_i) \\
 & + \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} \\
 & \times \left\{ \sum_b z_b \left[N_n(\bar{X}_i) \bar{C}_n^{b(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} \right] \right\} = 0 \tag{4.10}
 \end{aligned}$$

$$\begin{aligned} \bar{C}^{f(t+\Delta t)}(X_i) &= \frac{\phi_0^s \bar{C}_{s,0}^f(X_i) \bar{K}(X_i)}{\bar{K}(X_i) + \left[N_n(\bar{X}_i) \bar{C}_n^b + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} \right]} \end{aligned} \quad (4.11)$$

where

$$\begin{aligned} \bar{K}^{(t+\Delta t)}(X_i) &= \bar{K}_0 \\ &\times \exp \left[\frac{\bar{\alpha}_4 \sqrt{\frac{1}{2} \sum_b z_b^2 \left[N_n(\bar{X}_i) \bar{C}_n^{b(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} \right]}}{\left[1 + \bar{\alpha}_2 \sqrt{\frac{1}{2} \sum_b z_b^2 \left[N_n(\bar{X}_i) \bar{C}_n^{b(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} \right]}} \right]} \right] \end{aligned} \quad (4.12)$$

$$\begin{aligned} &(l+2m) \left\{ N_{n,XX}(\bar{X}_i) \bar{u}_n^{(t+\Delta t)} + 3 \left[M_m(\bar{X}_i) \bar{u}_{m,X}^{(t+\Delta t)} \right] \left[N_{n,XX}(\bar{X}_i) \bar{u}_n^{(t+\Delta t)} \right] \right\} \\ &+ \frac{3(l+2m)}{2} \left[M_m(\bar{X}_i) \bar{u}_{m,X}^{(t+\Delta t)} \right]^2 \left[N_{n,XX}(\bar{X}_i) \bar{u}_n^{(t+\Delta t)} \right] \\ &+ \frac{c_{ref} q F \bar{C}^{f(t+\Delta t)}(X_i) \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \left[N_{n,XX}(\bar{X}_i) \bar{u}_n^{(t+\Delta t)} \right]}{8\pi \varepsilon \kappa} \\ &- \frac{c_{ref} q F \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \frac{\partial \bar{C}^{f(t+\Delta t)}(X_i)}{\partial \bar{X}}}{8\pi \varepsilon r} \\ &- \frac{c_{ref} R T}{\lambda_1} \sum_b M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} = 0 \end{aligned} \quad (4.13)$$

where

$$\begin{aligned} \frac{\partial \bar{C}^{f(t+\Delta t)}(X_i)}{\partial \bar{X}} &= \frac{\phi_0^s \bar{C}_{s,0}^f(X_i) \bar{K}^{(t+\Delta t)}(X_i) \left[N_n(\bar{X}_i) \bar{C}_n^{b(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} \right]}{\left\{ \bar{K}^{(t+\Delta t)}(X_i) + \left[N_n(\bar{X}_i) \bar{C}_n^{b(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} \right] \right\}^2} \end{aligned} \quad (4.14)$$

The auxiliary equations required by the Hermite-cloud method at time $t + \Delta t$ are given as

$$N_{n,X}(\bar{X}) \bar{C}_n^{a(t+\Delta t)} - \left(N_{n,x}(\bar{X}) \bar{X}_n \right) M_m(\bar{X}) \bar{C}_{m,X}^{a(t+\Delta t)} = 0 \quad (4.15)$$

$$N_{n,X}(\bar{X})\bar{\psi}_n^{(t+\Delta t)} - \left(N_{n,x}(\bar{X})\bar{X}_n \right) M_m(\bar{X})\bar{\psi}_{m,X}^{(t+\Delta t)} = 0 \quad (4.16)$$

$$N_{n,X}(\bar{X})\bar{u}_n^{(t+\Delta t)} - \left(N_{n,x}(\bar{X})\bar{X}_n \right) M_m(\bar{X})\bar{u}_{m,X}^{(t+\Delta t)} = 0 \quad (4.17)$$

The Neumann boundary conditions (3.8) at time $t + \Delta t$ are discretized as

$$0 = M_m(\bar{X}_0)\bar{C}_{m,X}^{a(t+\Delta t)} \quad (4.18)$$

$$0 = M_m(\bar{X}_0)\bar{\psi}_{m,X}^{(t+\Delta t)} \quad (4.19)$$

$$\frac{T_0}{l + 2m} = M_m(\bar{X}_{MP})\bar{u}_{m,X}^{(t+\Delta t)} \quad (4.20)$$

and the Dirichlet boundary conditions (3.8) at time $t + \Delta t$ are discretized as

$$c_0^a = N_n(\bar{X}_{NP})\bar{C}_n^{a(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_{NP})\bar{X}_n \right) M_m(\bar{X}_{NP})\bar{C}_{m,X}^{a(t+\Delta t)} \quad (4.21)$$

$$0 = N_n(\bar{X}_{NP})\bar{\psi}_n^{(t+\Delta t)} + \left(\bar{X}_{NP} - \sum_{n=1}^{N_p} N_n(\bar{X}_{NP})\bar{X}_n \right) M_m(\bar{X}_{NP})\bar{\psi}_{m,X}^{(t+\Delta t)} \quad (4.22)$$

$$0 = N_n(\bar{X}_0)\bar{u}_n^{(t+\Delta t)} + \left(\bar{X}_0 - \sum_{n=1}^{N_p} N_n(\bar{X}_0)\bar{X}_n \right) M_m(\bar{X}_0)\bar{u}_{m,X}^{(t+\Delta t)} \quad (4.23)$$

Eqs. (4.9)-(4.23) constitute the complete nonlinear discrete system at time $t + \Delta t$. According to the Newton-Raphson method, the residuals of the discrete system are given as

$$\begin{aligned}
 R_{chem}^{a(t+\Delta t)} = & \bar{C}^{a(t+\Delta t)} - \\
 & \frac{\gamma \bar{D}^{a(t+\Delta t)} \bar{\beta}^{a(t+\Delta t)}}{\lambda_1^2} \left[N_n(\bar{X}_i) \bar{C}_n^{a(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t+\Delta t)} \right] \\
 & \times \left[\frac{1}{2} \sum_b z_b^2 N_{n,XX}(\bar{X}_i) \bar{C}_n^{b(t+\Delta t)} \right] \\
 & + \frac{\gamma \bar{D}^{a(t+\Delta t)}}{\lambda_1^2} \bar{\beta}^{a(t+\Delta t)}(\bar{I}) \left[M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t+\Delta t)} \right] \left[\frac{1}{2} \sum_b z_b^2 M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} \right] \\
 & + \frac{\gamma \bar{D}^{a(t+\Delta t)}}{\lambda_1^2} N_{n,XX}(\bar{X}_i) \bar{C}_n^{a(t+\Delta t)} \\
 & + \frac{z_a \theta \gamma \bar{D}^{a(t+\Delta t)}}{\lambda_1^2} \left[N_n(\bar{X}_i) \bar{C}_n^{a(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t+\Delta t)} \right] \\
 & \times \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n^{(t+\Delta t)} \right] \\
 & + \frac{z_a \theta \gamma \bar{D}^{a(t+\Delta t)}}{\lambda_1^2} \left[M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t+\Delta t)} \right] \left[M_m(\bar{X}_i) \bar{\psi}_{m,X}^{(t+\Delta t)} \right] \\
 & - \bar{C}^{a(t)} + \frac{\gamma \bar{D}^{a(t)} \bar{\beta}^{a(t)}}{\lambda_1^2} \left[N_n(\bar{X}_i) \bar{C}_n^{a(t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t)} \right] \times \\
 & \left[\frac{1}{2} \sum_b z_b^2 N_{n,XX}(\bar{X}_i) \bar{C}_n^{b(t)} \right] \\
 & - \frac{\gamma \bar{D}^{a(t)}}{\lambda_1^2} \bar{\beta}^{a(t)}(\bar{I}) \left[M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t)} \right] \left[\frac{1}{2} \sum_b z_b^2 M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t)} \right] \\
 & - \frac{\gamma \bar{D}^{a(t)}}{\lambda_1^2} N_{n,XX}(\bar{X}_i) \bar{C}_n^{a(t)} \\
 & - \frac{z_a \theta \gamma \bar{D}^{a(t)}}{\lambda_1^2} \left[N_n(\bar{X}_i) \bar{C}_n^{a(t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t)} \right] \\
 & \times \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n^{(t)} \right] \\
 & - \frac{z_a \theta \gamma \bar{D}^{a(t)}}{\lambda_1^2} \left[M_m(\bar{X}_i) \bar{C}_{m,X}^{a(t)} \right] \left[M_m(\bar{X}_i) \bar{\psi}_{m,X}^{(t)} \right]
 \end{aligned} \tag{4.24}$$

$$\begin{aligned}
 R_{elec}^{(t+\Delta t)} = & \frac{\varepsilon}{\lambda_1} \left[N_{n,XX}(\bar{X}_i) \bar{\psi}_n^{(t+\Delta t)} \right] + \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} z_f \bar{C}^{f(t+\Delta t)}(X_i) \\
 & + \frac{F^2 c_{ref} L_{ref}^2}{\theta R T} \\
 & \times \left\{ \sum_b z_b \left[N_n(\bar{X}_i) \bar{C}_n^{b(t+\Delta t)} + \left(\bar{X}_i - \sum_{n=1}^{N_p} N_n(\bar{X}_i) \bar{X}_n \right) M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)} \right] \right\}
 \end{aligned} \tag{4.25}$$

$$\begin{aligned}
 R_{mech}^{(t+\Delta t)} &= (\lambda + 2\mu) \\
 &\times \left\{ N_{n,XX}(\bar{X}_i) \bar{u}_n^{(t+\Delta t)} + 3 \left[M_m(\bar{X}_i) \bar{u}_{m,X}^{(t+\Delta t)} \right] \left[N_{n,XX}(\bar{X}_i) \bar{u}_n^{(t+\Delta t)} \right] \right\} \\
 &+ \frac{3(l+2m)}{2} \left[M_m(\bar{X}_i) \bar{u}_{m,X}^{(t+\Delta t)} \right]^2 \left[N_{n,XX}(\bar{X}_i) \bar{u}_n^{(t+\Delta t)} \right] \\
 &+ \frac{c_{ref} q F \bar{C}^{f(t+\Delta t)}(X_i)}{8\pi\epsilon\kappa} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \left[N_{n,XX}(\bar{X}_i) \bar{u}_n^{(t+\Delta t)} \right] \\
 &- \frac{c_{ref} q F}{8\pi\epsilon r} \left(\frac{\kappa + \lambda_1 r}{\lambda_1^2 \kappa} \right) \exp \left(-\frac{\lambda_1 r}{\kappa} \right) \frac{\partial \bar{C}^{f(t+\Delta t)}(X_i)}{\partial \bar{X}} - \frac{c_{ref} R T}{\lambda_1} \sum_b M_m(\bar{X}_i) \bar{C}_{m,X}^{b(t+\Delta t)}
 \end{aligned} \tag{4.26}$$

$$R_{auxi}^{a(t+\Delta t)} = N_{n,X}(\bar{X}) \bar{C}_n^{a(t+\Delta t)} - (N_{n,x}(\bar{X}) \bar{X}_n) M_m(\bar{X}) \bar{C}_{m,X}^{a(t+\Delta t)} \tag{4.27}$$

$$R_{auxi}^{elec(t+\Delta t)} = N_{n,X}(\bar{X}) \bar{\psi}_n^{(t+\Delta t)} - (N_{n,x}(\bar{X}) \bar{X}_n) M_m(\bar{X}) \bar{\psi}_{m,X}^{(t+\Delta t)} \tag{4.28}$$

$$R_{auxi}^{mech(t+\Delta t)} = N_{n,X}(\bar{X}) \bar{u}_n^{(t+\Delta t)} - (N_{n,x}(\bar{X}) \bar{X}_n) M_m(\bar{X}) \bar{u}_{m,X}^{(t+\Delta t)} \tag{4.29}$$

The incremental vector of the chemical, electrical and mechanical field variables and their corresponding first-order derivatives at time $t + \Delta t$ is given as

$$\left\{ \delta w^{t+\Delta t} \right\} = \begin{bmatrix} \delta \bar{C}^{a(t+\Delta t)} \\ \delta \bar{\psi}^{(t+\Delta t)} \\ \delta \bar{u}^{(t+\Delta t)} \\ \delta \bar{C}_{,X}^{a(t+\Delta t)} \\ \delta \bar{\psi}_{,X}^{(t+\Delta t)} \\ \delta \bar{u}_{,X}^{(t+\Delta t)} \end{bmatrix} \tag{4.30}$$

By taking the derivatives of the residuals with respect to the field variables and their derivatives, the Jacobian matrix at time $t + \Delta t$ is obtained as

$$J_{ij}^{(t+\Delta t)} = \frac{\partial R_i^{(t+\Delta t)}}{\partial w_j^{(t+\Delta t)}} \tag{4.31}$$

where $R_i^{(t+\Delta t)}$ is the i th residual function, and $w_j^{(t+\Delta t)}$ is the j th field variable at time $t + \Delta t$. The matrix form of the system is thus written as,

$$J_{ij}^{(t+\Delta t)} \delta w_j^{(t+\Delta t)} = -R_i^{(t+\Delta t)} \tag{4.32}$$

After imposing the boundary and initial conditions, the linear algebra system (4.32) can be solved by direct or indirect solvers. After each step of Newton iteration, the solution is updated at time $t + \Delta t$ by

$$w_i^{n+1(t+\Delta t)} = w_i^{n(t+\Delta t)} + \delta w_i^{(t+\Delta t)} \tag{4.33}$$

where n is the iterative step at time $t + \Delta t$. The convergence criterion is the same as shown in Eqn. (3.46).

4.2.4. Transient Algorithm

The complete transient algorithm of the MECis model is implemented as follows.

- (A). Inputting physical and chemical parameters, the boundary conditions, and time domain;
- (B). Calculating the initial variables for time step $t + \Delta t$;
- (C). Coupled solution for time step $t + \Delta t$;
 1. Calculating the fixed charge density distribution;
 2. Solving the chemical and electric fields at the coupled iteration step $n + 1$:
 - a. Estimating solution $\bar{C}_{new}^a = \bar{C}_n^a$, $\bar{\psi}_{new} = \bar{\psi}_n$;
 - b. Calculating the Jacobian matrix and right-hand side;
 - c. Imposing the Dirichlet and/or Neumann boundary conditions;
 - d. Solving $\Delta \bar{C}^a$ and $\Delta \bar{\psi}$;
 - e. Updating the solution, $\bar{C}_{new}^a \leftarrow \bar{C}_{old}^a + \Delta \bar{C}^a$, $\bar{\psi}_{new} \leftarrow \bar{\psi}_{old} + \Delta \bar{\psi}$;
 - f. Checking the convergence criterion, if not met, go to Step 2(b);
 3. Calculating osmotic pressure and electrical repulsive force;
 4. Solving the mechanical field at the coupled iteration step $n + 1$:
 - a. Estimating next solution $\bar{u}_{new} = \bar{u}_n$;
 - b. Calculating the Jacobian matrix and right hand side;
 - c. Imposing the Dirichlet and/or Neumann boundary conditions;
 - d. Solving $\Delta \bar{u}$;
 - e. Updating solution, $\bar{u}_{new} \leftarrow \bar{u}_{old} + \Delta \bar{u}$;
 - f. Checking the convergence criterion, if not met, go to Step 4(b);
 5. Updating the displacements, $u^{n+1} = u_{new}$;
 6. Checking the convergence for u^{n+1} and u^n , if not met, updating counter $n \leftarrow n + 1$, go to Step 1;
- (D). Updating time, $t \leftarrow t + \Delta t$;
- (E). Output the results, if t is less than the specified final time, go to Step (B).

4.2.5. Kinetic Swelling Ratio

The kinetic swelling ratio $SR(t)$ is defined as the volume ratio of the hydrogel with time t , namely,

$$SR(t) = \frac{V_t}{V_0} \quad (4.34)$$

where V_t and V_0 are the volumes of the hydrogel at time t and dry state, respectively. If the hydrogel is in disk or cylindrical shape, the kinetic swelling ratio can be further expressed as

$$SR(t) = \frac{d_t^2}{d_0^2} \quad (4.35)$$

where d_t and d_0 are the diameters of the hydrogel at time t and dry state, respectively.

In addition, the hydration of the hydrogel is defined as

$$H(t) = \frac{V_t - V_0}{V_0} = \frac{d_t^2}{d_0^2} - 1 \quad (4.36)$$

where $H(t)$ is the local hydration of the hydrogel at time t .

4.2.6. Diffusion Coefficient

As well known, the diffusivities of the mobile ions inside the hydrogel may vary with swelling/shrinking. There are several methods to track the change of the diffusivities. In this chapter, the obstruction model is applied as (De *et al.*, 2002),

$$D_h^a(t) = \left(\frac{H(t)}{H(t) + 2} \right)^2 D^a \quad (4.37)$$

where $D_h^a(t)$ is the diffusivity inside the hydrogel at time t .

4.3. Examination of the Transient MECis Model

In this section, the MECis model is examined for the kinetic swelling ratio of the ionic-strength-sensitive hydrogel by comparison of the MECis simulation results with the published experimental data for four types of hydrogels, namely, the hydroxypropyl methacrylate, *N,N*-dimethylaminoethylmethacrylate, and tetra-ethyl-

eneglycol dimethacrylate (HMDT) (Lin *et al.*, 2009), chitosan and poly(methacrylic acid) (CPMA) (Chen *et al.*, 2005), sodium methacrylate (SMA) (Jeon *et al.*, 1998), and 2-Hydroxyethylmethacrylate-co-Vinylbenzyltrimethyl-ammonium Chloride (HEMA-VBT) (Goel *et al.*, 2006a). The reversible kinetics is investigated for the HMDT and CPMA hydrogels; for the SMA and HEMA-VBT hydrogels however, the shrinking kinetics is studied.

4.3.1. Kinetic Reversible Swelling/Shrinking of HMDT

In the experimental work of Lin *et al.* (2009), the HMDT hydrogel was prepared by hydroxypropyl methacrylate (HPMA), *N,N*-dimethylaminoethylmethacrylate (DMA), and tetra-ethyleneglycol dimethacrylate (TEGDMA) (Lin *et al.*, 2009). The synthesized hydrogel was placed in a cylindrical sensing area with confinement condition in the radial direction (Lin *et al.*, 2009). The hydrogel with thickness of $400\mu\text{m}$ can thus only deform in the axial direction (Lin *et al.*, 2009), such that the problem can be simplified to one-dimensional domain. The chemical and physical parameters as the simulation input are given as follows. The initial fixed charge density is $C_{s,0}^f = 7.5\text{M}$ (Lin *et al.*, 2009), Young's modulus $E_Y = 0.7\text{MPa}$ (Pascual *et al.*, 1999), dissociation constant $pK = 6.17$, diffusivity of sodium $D^{Na^+} = 1.33 \times 10^{-9}\text{m}^2/\text{s}$, diffusivity of chlorine $D^{Cl^-} = 2.03 \times 10^{-9}\text{m}^2/\text{s}$, as tabulated in Table 4.1.

The simulation results and the corresponding experimental data are plotted in Fig. 4.2 for the reversible kinetics of the HMDT hydrogel in response to the ionic strength of surrounding solution. The solid lines represent the simulation results, and square markers the experimental data. The HMDT hydrogel is first immersed in a solution with an ionic strength of 150mM and reaches a dynamic equilibrium, where the concentrations of the mobile ions inside the hydrogel are around 150mM, and the osmotic pressure as well as repulsive force are balanced by elastic stretching. The ionic strength decreases rapidly to 50mM after $t = 0$. The osmotic pressure from the interior hydrogel to the external solution therefore decreases, and the balance is broken. The hydrogel has to stretch itself to equilibrate the increase of the osmotic pressure. Meanwhile, the diffusion of the mobile ions leads to the ionic movement from the interior hydrogel to the external solution, and lowers the osmotic pressure over the

hydrogel-solution interface.

The hydrogel then reaches a new equilibrium at $t = 24 \text{ min}$, where the concentrations of the mobile ions are around 50mM. However, the ionic strength increased rapidly again to 150mM at that instance. The osmotic pressure from the external solution to the interior hydrogel increases, and the hydrogel has to shrink to balance the increase of the osmotic pressure. Meanwhile, the concentration gap over the hydrogel-solution interfaces drives the mobile ions to move from the external solution into the hydrogel, and this decreases the difference of the osmotic pressure, until the hydrogel reaches the dynamic equilibrium. After $t = 46 \text{ min}$, the ionic strength decreases to 50mM again, and the hydrogel swells accordingly to balance the environmental change. After $t = 75 \text{ min}$, the ionic strength increases back to 150mM and the hydrogel shrinks once again. This swelling-shrinking reversible cycle continues repeatedly with time convolution.

The analysis shows that the MECis model predicts the swelling-shrinking reversible cycle, which is induced by the change of the environmental ionic strength, quite well.

4.3.2. Kinetic Reversible Swelling/Shrinking of CPMA

In order to compare with the experimental work of CPMA hydrogel synthesized from chitosan and poly(methacrylic acid) (Chen *et al.*, 2005), the chemical and physical parameters as the simulation input are given as follows. The initial fixed charge density is $C_{s,0}^f = 1110 \text{ mM}$ (Chen *et al.*, 2005), Young's modulus $E_Y = 87 \text{ MPa}$ (Chen *et al.*, 2009; Sedlackova *et al.*, 2001), dissociation constant $pK = 4.43$, diffusivity of natrium $D^{Na^+} = 1.33 \times 10^{-9} \text{ m}^2/\text{s}$, and diffusivity of chlorine $D^{Cl^-} = 2.03 \times 10^{-9} \text{ m}^2/\text{s}$. Other input parameters are shown in Table 4.2.

Fig. 4.3 illustrates the simulation results and the experimental data (Chen *et al.*, 2005) for the CPMA hydrogel responsive to the change of the ionic strength of the environmental solution. The two ionic strengths $I = 0.2 \text{ M}$ and $I = 2 \text{ M}$ are considered for the surrounding solution. The ionic strength changes from 0.2M to 2M at time $t = 4 \text{ h}$ and $t = 8.2 \text{ h}$, and from 2M to 0.2M at time $t = 6 \text{ h}$ and $t = 12 \text{ h}$. It is observed from Fig. 4.3 that the hydrogel shrinks when the ionic strength of the surrounding solution varies from 0.2M to 2M, while the hydrogel swells if the ionic

strength changes from 2M to 0.2M. The hydrogel reaches the equilibrium state at time $t = 4\text{h}$ when the ionic strength is equal to 0.2M. At this state, the elastic stress of the solid phase is balanced with the osmotic pressure and the electrical repulsive force. A step change of the ionic strength from 0.2M to 2M alters the ionic distribution outside the hydrogel, and produces the osmotic pressure from the interior hydrogel to the external solution. In order to equilibrate the osmotic pressure and the electrical repulsive force, the elastic stress of the solid phase also reduces, and thus the hydrogel shrinks until it reaches the equilibrium state.

At time $t = 6\text{h}$, when the hydrogel almost reaches equilibrium, the change of ionic strength from 2M to 0.2M breaks the balance, and produces an osmotic pressure from the external solution to the interior hydrogel. The osmotic pressure drives the hydrogel to swell until time $t = 8.2\text{h}$. Following this way, the change of the environmental ionic strength induces the swelling and shrinking reversibly.

The discrepancy between the experiments and simulations of the present model may be due to the slightly larger diffusion coefficients used. It may also come from the fact that the influence of the pH of the solution is not considered in the present model.

4.3.3. Kinetic Shrinking of SMA

In the experiment (Jeon *et al.*, 1998), the SMA hydrogel was synthesized by sodium methacrylate (SMA), where the SMA hydrogel was firstly immersed into a large amount of distilled water for full swelling and then placed to the solution with different ionic strengths ($I = 0.28, 0.1, 0.5, 2.3\text{M}$). Based on the experiment, the physical and chemical parameters are listed in Table 4.3.

The shrinking behavior of the SMA hydrogel is investigated by the MECis model and experiments (Jeon *et al.*, 1998). The simulation results from the MECis model and the experimental data are depicted in Fig. 4.4 for the kinetic shrinking behavior of the SMA hydrogel. As discussed in Chapter 3, the ionic-strength-sensitive hydrogel swells with the decrease of environmental ionic strength. The swelling ratio is at a maximum when ionic strength is zero. If the ionic strength is increased to a value larger than zero, the hydrogel shrinks. As is well known however for the kinetics of the hydrogel, the swelling and shrinking kinetics depend mainly on the diffusion of the ionic species and fluid. Initially, the concentrations of the ionic species inside the hydrogel are almost zero, relatively to that in the external solution. The osmotic pressure from the external

solution to the interior hydrogel due to the ionic concentration gap drives the hydrogel to shrink. Meanwhile, the concentration gap also drives the ions to move from the solution into the hydrogel. With the diffusion therefore, the concentration difference between the interior hydrogel and external solution decreases, and thus the driving force also decreases. The hydrogel reaches its dynamic equilibrium when the driving force is balanced by the elastic force.

It is also seen from Fig. 4.4 that, with the increase of the ionic strength, the hydrogel takes more time to reach the equilibrium state, and the equilibrium swelling ratio of the hydrogel decreases. The increase of the ionic strength reduces the mobility due to the gradient of the ionic strength. With larger ionic strength, the hydrogel has more difficulty in reaching equilibrium if the diffusion rate remains the same, and thus the hydrogel shrinks more drastically when it reaches the equilibrium state.

As shown in Fig. 4.4, when time $t < 10$ min, the shrinking predicted theoretically is relatively slower than that observed experimentally. The diffusivities of the ions determine the rate of the diffusion process, and thus control the kinetic response of the hydrogel. In the present comparison, the diffusion coefficients of the ionic sodium and chlorine are taken as those in the sodium chloride solution ($D^{Na^+} = 1.33 \times 10^{-9} \text{ m}^2/\text{s}$, $D^{Cl^-} = 2.03 \times 10^{-9} \text{ m}^2/\text{s}$). The mixture of the hydrogel with interstitial fluid may reduce the diffusion coefficients, such that the predicted shrinking is slightly faster than that in the experiment.

4.3.4. Kinetic Shrinking of HEMA-VBT

The HEMA-VBT hydrogel was prepared experimentally by 2-Hydroxyethyl methacrylate (HEMA) and Vinylbenzyltrimethylammonium chloride (VBT) (Goel *et al.*, 2006a), where it was synthesized to form a thin disk with diameter of 2cm and thickness of 0.6mm (Goel *et al.*, 2006a). The input data of various physical and chemical parameters for the simulation are tabulated in Table 4.4.

The HEMA-VBT hydrogel is first immersed into pure water for 650 minutes until it fully swells. After $t > 650$ min, the hydrogel is placed into a NaCl solution with the ionic strength of 0.1M. The hydrogel starts to shrink, as shown in Fig. 4.5. Due to the large difference of the osmotic pressure between the external solution and interior hydrogel, the shrinking is very fast in the first several minutes. Based on the MECis

model, the electrical, the chemical, and the mechanical fields try to reach an equilibrium state. The elastic stretching adjusts itself to balance the osmotic pressure and the electrical repulsive force. The mobile ions are driven by the electrical and chemical fields, and the movement reduces the difference of the osmotic pressure. The reduction of the osmotic pressure influences the elastic stretching. The whole process is cyclic, during which the elastic stretch becomes smaller and smaller, until the hydrogel and the solution reach the equilibrium state again in the new solution at about $t = 950\text{min}$.

After $t > 950\text{min}$, the hydrogel and the solution are in an equilibrium state, where the effects of the electrical and chemical as well as mechanical fields are balanced. The comparison shows that the MECis model can predict the kinetic shrinking of the HEMA-VBT hydrogel with good agreement.

4.4. Parameter Studies

In this section, the kinetic behavior of the ionic-strength-sensitive hydrogel is analyzed in the chemical, electrical, and mechanical coupled fields. The three parameter studies are carried out in order to improve the understanding of the influence of various environmental conditions or physical and chemical material parameters on the kinetic characteristics of the hydrogel. They include the reversible kinetics, the initial fixed charge density and Young's modulus. These parameter studies illustrate how the chemical, electrical and mechanical fields govern the kinetic swelling/shrinking behavior of the hydrogel, and demonstrate the kinetic characteristics of the mobile ionic concentration, the fixed charge density, the electric potential, and the displacement.

4.4.1. Analysis of Reversible Kinetics

The reversible kinetics of the smart hydrogel is widely applied in engineering and science experimentally. However, it is difficult for experiments to provide the magnitudes of several parameters/variables inside the hydrogel, such as the ionic concentrations and the electric potential, though several theories are able to provide predictions (Grimshaw *et al.*, 1990; Wallmersperger *et al.*, 2001a). Therefore, in order to study the transient characteristics of smart hydrogels responsive to the ionic strength in a reversible swelling-shrinking cycle, the simulation is carried out in this subsection

with the following representative parameters: the initial fixed charge density $C_{s,0}^f = 0.5\text{M}$, Young's modulus $E = 0.5\text{MPa}$, the dissociation constant $pK_0 = 3.5$, the diffusivities of positive ions $D^+ = 1.0 \times 10^{-7} \text{m/s}^2$ and negative ions $D^- = 1.0 \times 10^{-7} \text{m/s}^2$.

The predicted reversible swelling-shrinking cycles are shown in Fig. 4.6, where the response of the smart hydrogel is induced by the variation of the ionic strength from 2000mM to 10mM and vice versa. The hydrogel is immersed in a solution first with an ionic strength of 2000mM, and reaches dynamic equilibrium, where the concentrations of the mobile ions are around 2000mM. After $t = 0$, the ionic strength of the bathing solution dropped to 10mM. The initial profiles of the field variables, including the ionic concentrations (C^+ and C^-), the fixed charge density C^f , the electric potential ψ and the displacement u , are given as shown in Fig. 4.7. The step change of the ionic strength of the external solution breaks the equilibrium, making the concentrations of the mobile ions C^+ and C^- in the hydrogel much higher than those in the solution. The higher ionic concentrations inside the hydrogel drive the mobile ions to diffuse into the solution, as seen in Figs. 4.7(a)-(b) and 4.8(a)-(b), and thus the concentrations decrease with time. The ionic movement is much faster before 12min, and becomes slower after 12min. Meanwhile, the decrease of the positive ionic concentration C^+ inside the hydrogel breaks the binding equilibrium between the positive mobile ions and the negative fixed charges, and activates the dissociation of the fixed charge groups, resulting in the increase of the fixed charges C^f on the polymeric chains, as shown in Figs. 4.7(c) and 4.8(c). The different diffusivities of the ionic species and the existence of the fixed charges in the hydrogel result in the discrepancy between the positive and negative charge densities, which generates the electric potential ψ . With the increase of the fixed charges density C^f in the hydrogel, the discrepancy also increases and thus the electric potential ψ increases in the negative direction, as shown in Figs. 4.7(d) and 4.8(d).

The decrease of the ionic strength of the bathing solution increases the osmotic pressure from the interior hydrogel to the external solution, and thus the hydrogel stretches to balance the osmotic pressure and electrical repulsive force, as shown in Figs. 4.7(e) and 4.8(e). However, the diffusion of the mobile ions reduces the osmotic

pressure, resulting in the decrease of the displacement u of the hydrogel with time evolution. When $t < 12\text{ min}$, the diffusion of the mobile ions, the fixed charge density, the electric potential and the displacement vary much faster with time evolution. After $t \geq 12\text{ min}$ however, the whole system almost reaches a dynamic equilibrium, and the field variables vary slowly until stillness, and then the kinetic swelling ratio $SR(t)$ of the hydrogel reaches a constant, as seen in Fig. 4.6. After the swelling process reaches the dynamic equilibrium at the ionic strength of 10mM, the field variables and the kinetic swelling ratio do not change further with time evolution.

When the hydrogel-solution system is in dynamic equilibrium with the ionic strength of 10mM, after $t = 40\text{ min}$, the ionic strength of external solution increases rapidly to 2000mM. At this stage, the ionic concentrations C^+ and C^- in the external solution are higher than those in the interior hydrogel. The concentration difference drives the mobile ions to diffuse into the hydrogel, such that the ionic concentrations C^+ and C^- inside the hydrogel increase, as shown in Figs. 4.9(a)-(b) and 4.10(a)-(b). The increment of the positive ions C^+ inside the hydrogel activates the binding reaction between the positive ions and the fixed charges, and thus the fixed charge density C^f decreases, as seen in Figs. 4.9(c) and 4.10(c). Meanwhile, the electric potential ψ rises and approaches zero due to the decrease of the discrepancy of the positive and negative charges inside the hydrogel, as shown in Figs. 4.9(d) and 4.10(d). The increase of the environmental ionic strength also enhances the osmotic pressure from the interior hydrogel to the external solution, which induces the hydrogel to shrink. The diffusion of the mobile ions enlarges the concentrations inside the hydrogel, and the osmotic pressure from the hydrogel to the solution thus increases with time evolution. Therefore, the displacement of the hydrogel u decreases with time, as shown in Figs. 4.9(e) and 4.10(e). Similar to the swelling process, the field variables in the shrinking process, including the ionic concentration, the fixed charge density, the electric potential and the displacement, vary much fast with time when $40\text{ min} < t < 52\text{ min}$, and become much slow when $52\text{ min} < t < 80\text{ min}$, since the hydrogel-solution system almost reaches a new equilibrium. After the system reaches the dynamical equilibrium at time $t = 60\text{ min}$, the field variables do not change any more. At the dynamic equilibrium state, the osmotic pressure, the elastic stress, and the electric repulsive force are in balance. The gradients of concentrations

and the electric potential, and the binding reaction between the fixed charges and mobile ions are all in dynamic equilibrium.

The equilibrium is lost again at $t = 80 \text{ min}$, when the ionic strength of the solution changes back to 10mM. The hydrogel almost follows the same swelling process as described above, with the change of the field variables with time evolution, and it reaches dynamic equilibrium again. At $t = 120 \text{ min}$, the ionic strength reverts to 2000mM. The hydrogel starts to shrink, and the shrinking process is also almost the same as discussed above, until the system reaches the new dynamic equilibrium. The reversible swelling-shrinking cycle can be further induced by the change of the external ionic strength.

Briefly, the ionic concentrations, the fixed charge density, the electric potential, and the displacement vary with time during the reversible swelling-shrinking cycle by changing the ionic strength of the bath solution. This analysis gives an insight to the variation of the physical and chemical quantities with time.

4.4.2. Influence of Initial Fixed Charge Density

The initial fixed charge density has significant influence on the kinetic swelling characteristics of the smart hydrogel, which is responsive to environmental ionic strength. In general, the ionic-strength-sensitive hydrogel with the larger initial fixed charge density swells more, if all the other conditions remain unchanged (Ali and Hegazy, 2007; Bajpai, 2001). In order to analyze the kinetic effect of the initial fixed charge density on the ionic-strength-sensitive hydrogel by the present MECis model, the three cases studies are conducted for the various initial fixed charge densities $C_{s,0}^f = 0.8, 1.6, 2.4 \text{ M}$, while the other input parameters are given as follows. The valance of the fixed charges is $z_f = -1$, the Young's modulus $E = 80 \text{ kPa}$, the dissociation constant $pK_0 = 6$, the diffusivities of the positive ion $D^+ = 1.0 \times 10^{-7} \text{ m}^2/\text{s}$, and the negative ions $D^- = 1.0 \times 10^{-7} \text{ m}^2/\text{s}$. In the simulation, the hydrogel is initially in the equilibrium state with the environmental ionic strength of 0.15M. Then the environmental ionic strength starts to decrease to 0.05M.

The simulation results for the influence of the initial fixed charge density C_0^f on

the kinetic swelling ratio $SR(t)$ of the ionic-strength-sensitive hydrogel are demonstrated in Fig. 4.11. As observed from the figure, the kinetic swelling ratio $SR(t)$ of the hydrogel increases with increasing initial fixed charge density C_0^f . Initially, the concentrations of the mobile ions inside the hydrogel C^+ and C^- are close to 0.15M, the fixed charge density C_0^f is 0.0027M, and the electric potential ψ is -0.25mV. They correspond to the steady-state solution when the ionic strength of the external solution is 0.15M. With time evolution, the concentrations of the mobile ions C^+ and C^- decrease inside the hydrogel, the mobile ions randomly diffuse into the external solution from the interior hydrogel. At the beginning, the concentrations of the mobile ions C^+ and C^- outside the hydrogel increase. However, they start to decrease after a few minutes, due to the limitation of the diffusion rate of the mobile ions. When the mobile ions diffuse into the external solution from the interior hydrogel, they cannot diffuse to the edge of external solution immediately, and thus accumulate around the hydrogel first and then move slowly to the boundary of the solution.

The binding reaction between the fixed charges and the positive mobile ions becomes less active if the concentration of the positive ions C^+ within the hydrogel decreases. The binding equilibrium is a state of balance between the bound process of the mobile ions and the dissociation process of the fixed charges. The equilibrium is lost when the mobile positive ions start to decrease. After time $t > 40$ min, the mobile ionic concentrations C^+ and C^- and the fixed charge density C^f as well as the electric potential ψ continuously vary and try to reach an equilibrium. The final state of the hydrogel is the equilibrium among the elastic stretching of the polymeric network, the osmotic pressure, and the electrical repulsive force. It is also a balance of the chemical and electric potential between the interior hydrogel and external solution. For example, the chemical potential μ may drive the positive ions to move towards outside the hydrogel, while the electric potential ψ may drive them to move towards inside the hydrogel. These two driving sources dynamically equilibrate each other when the hydrogel reaches equilibrium. In addition, the final state is an equilibrium between the dissociation of the fixed ionizable group and the binding of the mobile ions to the hydrogel, such that the final equilibrium state may be influenced by the initial fixed charge density.

The initial fixed charge density C_0^f plays a significant role in the swelling of the hydrogel. Firstly, the initial fixed charge density influences the diffusion rate of the mobile ions. Fig. 4.12 demonstrate the profiles of the mobile ionic concentrations C^+ and C^- , the fixed charge density C^f and the electric potential ψ for the three initial fixed charge densities at time $t = 15$ min. It is observed from Figs. 4.12(a) and (b) that the concentrations of the mobile ions are higher when the hydrogel has lower initial fixed charge density C_0^f . The observation proves that the diffusion of the mobile ions with higher initial fixed charge density is faster than that with lower initial fixed charge C_0^f . Fig. 4.12(d) illustrates that the higher initial fixed charge density C_0^f can produce greater absolute value of electric potential inside the hydrogel. Obviously, the reason is that the electric potential ψ is governed by the net charge density inside the hydrogel, and the net charge is contributed mainly by the fixed charge density C^f . The increase of electric potential ψ makes the mobile ions move faster towards the outside of the hydrogel, due to the electrostatic interaction between mobile ions. Therefore, with the increase of the initial fixed charge density C_0^f , the diffusion rate of the mobile ions also increases and thus less mobile ions are left in the hydrogel. In addition, the electrical repulsive force is governed by the initial fixed charge density. With a higher initial fixed charge density, the repulsive force increases, and thus the kinetic swelling ratio SR also increases, as observed in Fig. 4.12(e).

The initial fixed charge density C_0^f influences the concentration of the positive mobile ions C^+ differently, as seen in Fig. 4.13(a), where the lower initial fixed charge density reduces the concentration of the positive mobile ions C^+ . At equilibrium state, the larger initial fixed charge density leaves the more unbound fixed charges on the polymeric chains, as observed in Fig. 4.13(c), and thus produces a greater electric potential ψ inside the hydrogel, as seen in Fig. 4.13(d). Therefore, in order to resist the diffusion of the positive ions into the hydrogel due to the larger electric potential, the chemical potential of the positive ions inside the hydrogel has to become greater. The concentration of the positive ions C^+ thus increases with initial fixed charge density. In addition, the hydrogel system tries to maintain an electroneutrality state. As such, the concentration of the positive ions C^+ increases

when the initial fixed charge density C_0^f enlarges. If the concentrations of the positive ions C^+ , negative ions C^- and fixed charges C^f with their valances are summed up, a resulting value is almost equal to zero. These observations can also be validated by the equilibrium analysis of the influence of the initial fixed charge density in Chapter 3.

The above parameter study has provided a deep insight into the transient behavior of the smart hydrogel and the kinetic characteristics of the mobile ions and the fixed charges as well as the electric potential, when the hydrogel is placed in the solution with different ionic strengths. It is observed that the initial fixed charge density C_0^f has a trivial influence on the swelling rate of ionic-strength-sensitive hydrogels. However, it does have substantial effect on the physical and chemical quantities in the hydrogel and solution.

4.4.3. Influence of Young's Modulus

The influence of the Young's modulus on the kinetic swelling of the ionic-strength-sensitive hydrogel is investigated in this subsection. Four representative Young's moduli, $E = 0.2, 0.4, 0.6, 0.8 \text{ MPa}$, are analyzed. The other physical and chemical parameters are given as follows, the valance of the fixed charge $z_f = -1$, the initial fixed charge density $C_{s,0}^f = 500 \text{ mM}$, the dissociation constant $pK_0 = 3.5$, the diffusivity of the positive ion $D^+ = 1.0 \times 10^{-7} \text{ m}^2/\text{s}$, and the negative ion $D^- = 1.0 \times 10^{-7} \text{ m}^2/\text{s}$. The hydrogel is first immersed in a solution with an ionic strength of 1000mM thereafter reaching a dynamic equilibrium. Then the hydrogel is transferred to a solution with an ionic strength of 10mM. The kinetic swelling of the ionic-strength-sensitive hydrogel from the ionic strength of 1000mM to 10mM is simulated for analysis of the influence of the Young's modulus.

Fig. 4.14 shows the numerical simulation of kinetic swelling ratio SR as a function of time t and Young's modulus E . The swelling is very fast at the beginning, then becomes slower, and finally reaches a dynamic equilibrium. With the increase of the Young's modulus, the rate of kinetic swelling ratio SR decreases. This is confirmed by simply comparing the slope of each curve in the figure at the same time. At the initial time, the osmotic pressure and electrical repulsive force are

almost the same for the four hydrogels with different Young's moduli. Under the same driving forces, the larger Young's modulus E is, the smaller will be the elastic stretching. Therefore, the swelling rates increases by decreasing the Young's modulus E .

It is also observed from Fig. 4.14 that the hydrogel and solution easily reach the equilibrium state with a larger Young's modulus E , for example, 13, 10, 8, and 7.5 minutes for the hydrogel with Young's moduli $E = 0.2, 0.4, 0.6, \text{ and } 0.8 \text{ MPa}$. When the hydrogel is still swelling, the smaller Young's modulus makes the polymeric network stretch larger. After the driving force becomes small enough, a larger Young's modulus prevents the hydrogel from swelling any more, and the thermodynamic system of hydrogel and solution is thus equilibrated. However, subjected to the same small driving force, the polymeric network with a smaller Young's modulus may still have to stretch to reach a balance. Therefore, a smaller Young's modulus requires a longer time to reach the thermodynamic equilibrium. There is a step change of kinetic swelling ratio SR when the hydrogel is in equilibrium for the Young's modulus changed from 0.2MPa to 0.4MPa. The step change of the equilibrium swelling ratio ESR is also observed in the analysis of equilibrium swelling ratio ESR subjected to the influence of the Young's modulus in Subsection 3.4.4. The equilibrium swelling ratio ESR follows the exponential decrease with the increase of the Young's modulus, as shown in Subsection 3.4.4. From the kinetic point of view, the step change is due to the accumulation of the stretch at each time.

Fig. 4.15 illustrates the influence of Young's modulus on the kinetic distributions of the positive ion C^+ (a), the negative ion C^- (b), the fixed charge density C^f (c), the electric potential ψ (d), and the displacement u (e) at time $t = 5 \text{ min}$. The Young's modulus has less influence on the mobile ions at the initial stages as shown in Figs. 4.15(a) and (b), since the diffusions of the mobile ions are governed mainly by the chemical and electric fields. However, the fixed charge density C^f is largely dependent on the Young's modulus E as observed in Fig. 4.15(c). With almost the same concentrations of mobile ions and the equilibrium constants, the equilibrium reaction efficiency is determined mainly by the fixed charge sites. If the fixed charge sites distribute more widely in the hydrogel, namely the volume of the hydrogel becomes larger, the reaction efficiency is increased and the fixed charge density is thus decreased. However, the fixed charge density is increased with the increment of the

Young's modulus. The increase of the fixed charge density C^f also decreases the electric potential ψ , since the valence of the fixed charge is negative as shown in Fig. 4.15(d), with the almost unchanged concentrations of mobile ions. Fig. 4.15(e) presents the displacement profile as a function of Young's modulus, where Young's modulus influences the displacement directly. With the increase of the Young's modulus, the displacement decreases from the mechanical point of view.

In the equilibrium state at time $t = 35 \text{ min}$, the numerical simulation for the influence of Young's modulus on the kinetic distributions of the positive ion C^+ (a), the negative ion C^- (b), the fixed charge density C^f (c), the electric potential ψ (d), and the displacement u (e) are plotted in Fig. 4.16. The fixed charge density C^f and electric potential ψ display similar trends as observed above in Figs. 4.16(c)-(d). The electric field due to the fixed charges drives the mobile ions to equilibrate the fixed charges and electric potential. Therefore, the concentration of the positive ion C^+ increases with the increment of the Young's modulus E as seen in Fig. 4.16(a), while the concentration of the negative ion C^- decreases with the increment of the Young's modulus E , as seen in Fig. 4.16(b). The displacement profile u has the same trend as that at time $t = 5 \text{ min}$, as shown in Fig. 4.16(e). Since the hydrogel and solution are almost in equilibrium state, the displacement is very small when compared with the dimension of the hydrogel, and therefore is almost negligible.

In summary, this analysis provides a further understanding of the responsive characteristics of the ionic-strength-sensitive hydrogel with varying Young's moduli, including the deformation, the ionic concentration, fixed charge density and electrical potential. It is known that the Young's modulus has substantial influence not only on the final equilibrium state, but also on the swelling process and swelling rate.

4.5. Summary

In this chapter, the kinetic analysis of the ionic-strength-sensitive hydrogel is carried out by employing the transient MECis model.

The simulation results by the transient MECis model are compared with the published experimental work (Chen *et al.*, 2005; Goel *et al.*, 2006a; Jeon *et al.*, 1998; Lin *et al.*, 2009), for four types of hydrogels, HMDT, CPMA, SMA and HEMAVBT hydrogels, in response to the environmental ionic strength. The four types of hydrogels

represent different ionic-strength-sensitive hydrogels, with varying parameters consisting of Young's moduli, fixed charge densities, and equilibrium constants. The analyses of the four hydrogels cover the swelling, shrinking and reversible behaviors. A comparison with the theoretical and experimental works demonstrates that the present MECis model is robust to predict the swelling, shrinking and reversible kinetics of the ionic-strength-sensitive hydrogel, and accurate to trace the kinetic swelling ratio of the hydrogel.

The parameter studies are carried out for the kinetic analysis of the reversible swelling and shrinking, the influence of the initial fixed charge density and Young's modulus on the ionic-strength-sensitive hydrogel. The analysis of the reversible kinetics of the ionic-strength-sensitive hydrogel demonstrates how the thermodynamic characteristics vary during swelling-shrinking and the reverse cycles in the hydrogel-solution system, as the reversible large deformation without loss of network structure is one of the most important advantages of the smart hydrogel. The detailed investigation gives a full picture from nonequilibrium to equilibrium in the reversible cycle. In addition, the studies of the influence of the initial fixed charge density and Young's modulus on the kinetic ionic-strength-sensitive hydrogel illustrate how the kinetic swelling/shrinking proceeds with different chemical and physical parameters. The studies also present the chemical, electrical and mechanical profiles of the hydrogel, which are helpful in understanding the characteristics of the hydrogel subjected to the ionic-strength stimulus.

The present transient analyses of the ionic-strength-sensitive hydrogel with the MECis model promote the understanding of the hydrogel from a theoretical point of view. The comparisons and parameter studies demonstrate that, the MECis model, as an excellent tool, is capable of simulating the kinetics of the ionic-strength-sensitive hydrogel well.

Table 4.1. Physical and chemical parameters of HMDT hydrogel.

Parameters	Value
Diffusion coefficient of natrium ions D^{Na^+} (m / s ²)	1.33×10^{-9}
Diffusion coefficient of chlorine ions D^{Cl^-} (m / s ²)	2.03×10^{-9}
Environmental ionic strength $I(M)$ (Lin <i>et al.</i> , 2009)	$0.05 \leftrightarrow 0.15$
Initial diameter of hydrogel (mm) (Lin <i>et al.</i> , 2009)	0.4
Initial fixed charge density $C_{s,0}^f$ (mM) (Lin <i>et al.</i> , 2009)	7500
Initial fixed charge distance r_0 (nm)	30
Intrinsic dissociation constant pK_0 (M)	6.17
Temperature $T(K)$	298
Valence of fixed charge z_f	-1
Young's modulus $E(MPa)$ (Pascual <i>et al.</i> , 1999)	0.7

Table 4.2. Physical and chemical parameters of CPMA hydrogel.

Parameters	Value
Diffusion coefficient of natrium ions D^{Na^+} (m / s ²)	1.33×10^{-9}
Diffusion coefficient of chlorine ions D^{Cl^-} (m / s ²)	2.03×10^{-9}
Environmental ionic strength $I(M)$ (Chen <i>et al.</i> , 2005)	$0.2 \leftrightarrow 2$
Initial diameter of hydrogel (mm) (Chen <i>et al.</i> , 2005)	6
Initial fixed charge density $C_{s,0}^f$ (mM) (Chen <i>et al.</i> , 2005)	1110
Initial fixed charge distance r_0 (nm) (Bell and Peppas, 1996)	30
Intrinsic dissociation constant pK_0 (M)	4.43
Temperature $T(K)$	298
Valence of fixed charge z_f	-1
Young's modulus E (MPa) (Chen <i>et al.</i> , 2009; Sedlackova <i>et al.</i> , 2001)	87

Table 4.3. Physical and chemical parameters of SMA hydrogel.

Parameters	Value
Diffusion coefficient of natrium ions D^{Na^+} (m / s ²)	1.33×10^{-9}
Diffusion coefficient of chlorine ions D^{Cl^-} (m / s ²)	2.03×10^{-9}
Environmental ionic strength $I(M)$ (Jeon <i>et al.</i> , 1998)	0.028, 0.1, 0.5, 2.3
Initial fixed charge density $C_{s,0}^f$ (mM) (Jeon <i>et al.</i> , 1998)	37
Initial fixed charge distance r_0 (nm) (Bell and Peppas, 1996)	25
Intrinsic dissociation constant pK_0 (M)	4.43
Temperature $T(K)$	298
Valence of fixed charge z_f	-1
Young's modulus E (MPa) (Bdair <i>et al.</i> , 1993)	13

Table 4.4. Physical and chemical parameters of HEMA-VBA hydrogel.

Parameters	Value
Diffusion coefficient of natrium ions D^{Na^+} (m / s ²)	1.33×10^{-9}
Diffusion coefficient of chlorine ions D^{Cl^-} (m / s ²)	2.03×10^{-9}
Environmental ionic strength $I(M)$ (Goel <i>et al.</i> , 2006a)	$0 \rightarrow 0.1$
Initial diameter of hydrogel (mm) (Goel <i>et al.</i> , 2006a; Goel <i>et al.</i> , 2006b)	20
Initial fixed charge density $C_{s,0}^f$ (mM) (Goel <i>et al.</i> , 2006a; Goel <i>et al.</i> , 2006b)	4560
Initial fixed charge distance r_0 (nm)	300
Intrinsic dissociation constant $pK_0(M)$	5
Temperature $T(K)$	298
Valence of fixed charge z_f	-1
Young's modulus $E(MPa)$ (De <i>et al.</i> , 2002)	0.25

Fig. 4.1. Initial conditions for the numerical implementation of the MECis model, in which the electric potential ψ and fixed charge density C_0^f are initially equal to zero in the solution domain, and the concentrations of the mobile ions (C^+ and C^-) are equilibrated with the fixed charges C_0^f inside the hydrogel.

Fig. 4.2. Reversible kinetics of HMDT hydrogel subject to the reversible change of the ionic strength from 50 to 150mM by the MECis model and experiments (Lin *et al.*, 2009).

Fig. 4.3. Reversible kinetics of CPMA hydrogel subject to the reversible change of the ionic strength from 50 to 150mM by the MECis model and experiments (Chen *et al.*, 2005).

Fig. 4.4. Kinetic shrinking of SMA hydrogel subject to various ionic strengths ($I = 0.28, 0.1, 0.5, 2.3M$) by the MECis model and experiments (Jeon *et al.*, 1998).

Fig. 4.5. Kinetic shrinking of HEMA-VBT hydrogel subject to ionic strength ($I = 0.1M$) by the MECis model and experiments (Goel *et al.*, 2006a).

Fig. 4.6. Reversible kinetics of the hydrogel responsive to the ionic strength changing from 10 to 2000mM and vice versa.

Fig. 4.7. Predicted kinetic distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution by the MECis model, with time evolution during swelling when $t < 12$ min, where the arrows denote the time evolution.

Fig. 4.8. Predicted kinetic distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution by the MECis model, with time evolution during swelling when $t > 12$ min, where the arrows denote the time evolution.

Fig. 4.9. Predicted kinetic distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution by the MECis model, with time evolution during shrinking when $t < 12$ min, where the arrows denote the time evolution.

Fig. 4.10. Predicted kinetic distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u (e) in the hydrogel and solution by the MECis model, with time evolution during shrinking when $t > 12$ min, where the arrows denote the time evolution.

Fig. 4.11. Influence of the initial fixed charge density $C_{s,0}^f$ on the kinetic swelling ratio $SR(t)$ of the ionic-strength-sensitive hydrogel.

Fig. 4.12. Influence of the initial fixed charge density $C_{s,0}^f$ on the kinetic distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u in the hydrogel and solution, when time $t = 15$ min.

Fig. 4.13. Influence of the initial fixed charge density $C_{s,0}^f$ on the kinetic distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u in the hydrogel and solution, when time $t = 100 \text{ min}$.

Fig. 4.14. Influence of Young's modulus E on the kinetic swelling ratio $SR(t)$ of the ionic-strength-sensitive hydrogel.

Fig. 4.15. Influence of the Young's modulus E on the kinetic distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u in the hydrogel and solution, when time $t = 5$ min.

Fig. 4.16. Influence of the Young's modulus E on the kinetic distributions of the positive ion C^+ (a), negative ion C^- (b), fixed charge C^f (c), electric potential ψ (d), and displacement u in the hydrogel and solution, when time $t = 35$ min .

5

Finite Element Analysis for Gel and Dielectrics

5.1. Introduction

In this chapter, the finite element analysis is presented in two folds for the investigation of gels and dielectrics, respectively.

In Section 5.2, a gel placed in water with various transient deformation patterns is analyzed by the finite element model developed by Zhang *et al.* (2009), as presented in Subsection 5.2.2. This finite element model is based on the field theory proposed by Hong *et al.* (2008), as summarized in Subsection 5.2.1. In Section 5.2.3, we employ this finite element model to carry out the numerical simulations for investigation of the deformation of the constrained gel, the block gel, the thin film of gel, and the bonded gel, all of which are placed in the water, by the commercial software ABAQUS via its USER-ELEMENT subroutine (UEL). The different deformation patterns are analyzed and discussed in details, including the swelling, wrinkling, folding, twisting, waving, and buckling. We also conduct the experiments for observation of the deformation patterns of the cubic and thin film gels, where the wrinkling and waving patterns are observed. Then, the simulation results are compared with the experiments, and a good agreement is achieved. The contributions of the present study include the analysis of more types of gels and constrain to study different deformation patterns of the cubic gel, and experimental validation of the deformation patterns of cubic and thin film gels.

In Section 5.3, the deformation of dielectrics is studied by the finite element analysis. This study is based on the theory proposed by Suo *et al.* (2008), as summarized in Subsection 5.3.1. In Subsection 5.3.2, we develop a finite element formulation for the dielectrics problems, through the USER-ELEMENT subroutine (UEL) of the commercial software ABAQUS. The two problems are studied, as

described in Section 5.3.3, including the dielectrics subject to the electromechanical loads within and without solvent. As the first problem, the layers of the dielectrics subject to a voltage are studied with and without mechanical load. In the second problem, the dielectric gel immersed in a solvent is analyzed subjected to the electromechanical load. In addition, we also study the influence of different material parameters on the deformation of the dielectric gel in solvent. The finite element results are compared with the analytical solutions, and good agreements are obtained.

Finite element method (FEM) is a powerful numerical technique which is widely applied in engineering and science. FEM is able to achieve good approximate solutions for differential and integral equations. Further, the nonlinear FEM is an essential component for computer-aided engineering design. Currently the testing of prototypes is increasingly replaced by simulation with nonlinear FEM, which provides a more rapid and less expensive way to evaluate design concepts of the prototypes (Belytschko *et al.*, 2001). Recently, the increasing interest of FEM is extended to the simulations of soft materials such as hydrogel or polymer, in order to handle complicated geometry and boundaries. For instance, Suematsu *et al.* (1990) employed the three-dimensional explicit finite element model to investigate the pattern formation of swelling gel. Wallmersperger *et al.* (2008; 2002; 2001b; 2007) conducted a time-discontinuous Galerkin finite element analysis, which yields the implicit and unconditional stable solutions with higher-order accuracy, in order to simulate the ionic hydrogel in a solution with or without external electric field. Dolbow *et al.* (2004, 2005) presented a hybrid eXtended-finite-element/level-set method to study the deformation of hydrogel. Birgersson *et al.* (2008) analyzed the transient behavior of the two-dimensional temperature-sensitive hydrogel through the commercial finite element solver COMSOL MULTIPHYSICS. Westbrook and Qi (2008) developed a finite element model for gel at equilibrium state. Zhao and Suo (2008) investigated the deformation of dielectrics subject to the voltage, by embedding the material model into the USER-MATERIAL subroutine of the commercial finite element solver ABAQUS. Hong *et al.* (2009) studied the inhomogeneous swelling of gel in a solvent by coding the model into the USER-HYPERELASTICITY subroutine of ABAQUS. Zhang *et al.* (2009) developed a finite element model for transient analysis of the concurrent large deformation and mass transport in hydrogel, via the USER-ELEMENT subroutine of ABAQUS. Liu *et al.* (2010) analyzed the buckling of the thin film gels via the developed subroutine (Hong *et al.*, 2009). In brief, many studies have been conducted

using finite element methods with either commercial software or developed codes to explore the intriguing nature of various gels.

5.2. Transient Analysis of Gel in Solvent

When a gel is immersed in a solvent such as water, the solvent molecules migrate into the gel network, and interact either with one another or with the polymeric chains. The interaction induces swelling of the gel, and thus the decrease of the entropy of the network and the increase of the entropy of the mixture. In this section, the migration of the solvent molecules and the deformation of the gel are studied. This work is based on the field theory proposed by Hong *et al.* (2008) for the energy equilibrium and the kinetics of the gel in a solvent, as described in Subsection 5.2.1. It is followed by the finite element modeling developed by Zhang *et al.* (2009), as described in Subsection 5.2.2. In Subsection 5.2.3, we carry out numerical simulations for analysis of different deformation patterns of the various gels.

5.2.1. Field Theory Proposed by Hong et al.

Hong *et al.* (2008) proposed a field theory for the gel placed in the solvent with nonequilibrium thermodynamics and kinetic law. In this theory, the gel consisting of polymeric networks and small solvent molecules is considered as a thermodynamic system, as shown in Fig. 5.1, where the pumps maintain the chemical potential μ and do work to the gel by injecting the solvent molecules δC , and the weights maintain the force P , and do work to the system by stretching the gel δl . This theory describes the kinematics of the polymeric network, the definition of nominal stress, the conservation of small solvent molecules, the molecular incompressibility condition, the local equilibrium condition, the kinetics of migration, and the material model.

The field theory is developed in the reference configuration, where a marker of the gel occupies in the space with Lagrangian coordinate $\mathbf{X}$. The volume of the element around the marker $\mathbf{X}$ is denoted by $dV(\mathbf{X})$, and its surface by $N_k(\mathbf{X})dS(\mathbf{X})$, where $dS(\mathbf{X})$ is the area of the element and $N_k(\mathbf{X})$ is the unit vector normal to the surface. In a current configuration at time t , the marker $\mathbf{X}$ moves to a place with Eulerian coordinate $\mathbf{x}(\mathbf{X}, t)$.

The kinematics of the polymeric network is thus characterized by the deformation

gradient of the network $\mathbf{F}$ as

$$F_{iK} = \frac{\partial x_i(\mathbf{X}, t)}{\partial X_K} \quad (5.1)$$

If the force due to the weights in a control volume is $B_K(\mathbf{X}, t)dV$ and on the surface of the volume $T_K(X, t)dS$, the definition of nominal stress P_{iK} for any test function $\xi_i(\mathbf{X})$ is given as

$$\int P_{iK} \frac{\partial \xi_i}{\partial X_K} dV = \int B_i \xi_i dV + \int T_i \xi_i dS \quad (5.2)$$

By applying the divergence theorem, the above Eqn. (5.2) leads to

$$\int P_{iK} N_K \xi_i dS - \int \frac{\partial P_{iK}}{\partial X_K} \xi_i dV = \int B_i \xi_i dV + \int T_i \xi_i dS \quad (5.3)$$

Due to the arbitrariness of the test function and the control volume, Eqn. (5.3) is rewritten as

$$\frac{\partial P_{iK}(\mathbf{X}, t)}{\partial X_K} + B_i(\mathbf{X}, t) = 0 \quad (\text{In the volume}) \quad (5.4)$$

$$P_{iK}(\mathbf{X}, t) N_K(\mathbf{X}, t) = T_i(\mathbf{X}, t) \quad (\text{On the surface}) \quad (5.5)$$

The definition of nominal stress leads to a classical equation for force balance in the continuum mechanics.

In addition, if $C(\mathbf{X}, t)$ is the nominal concentration of the solvent in the gel, $C(\mathbf{X}, t)dV$ is the number of solvent molecules in the control volume, and the number of the molecules injected into the control volume per unit time is denoted by $r(\mathbf{X}, t)dV$, and into the surface by $i(\mathbf{X}, t)dS$, the conservation of solvent molecules requires that the number of solvent molecules obeys

$$\frac{\partial C(\mathbf{X}, t)}{\partial t} + \frac{\partial J_K(\mathbf{X}, t)}{\partial X_K} = r(\mathbf{X}, t) \quad (\text{In the volume}) \quad (5.6)$$

$$J_K(\mathbf{X}, t) N_K(\mathbf{X}, t) = i(\mathbf{X}, t) \quad (\text{On the surface}) \quad (5.7)$$

where $J_K(\mathbf{X}, t)$ is the nominal flux of the solvent molecules.

Eqs. (5.6) and (5.7) can also be expressed in an integration form through multiplying an arbitrary test function $\zeta(\mathbf{X})$ in both the sides of the equations, and then integrating over the control volume and surface as

$$\int \frac{\partial C}{\partial t} \zeta dV = \int J_K \frac{\partial \zeta}{\partial X_K} dV + \int r \zeta dV + \int i \zeta dS \quad (5.8)$$

In this theory, it is assumed that the individual polymer chain and solvent molecule are incompressible, and the gel system is a condensed matter without void space, namely the configuration is occupied by either polymeric chains or solvent molecules. These assumptions lead to the molecular incompressibility condition as

$$1 + vC = \det(\mathbf{F}) \quad (5.9)$$

where v is the volume of per solvent molecule.

In the thermodynamic system shown in Fig. 5.1, it is assumed that the free energy density of the gel W is only a function of the deformation gradient $\mathbf{F}$ and the nominal concentration of solvent C . With the small change of the deformation gradient δF_{iK} and nominal concentration δC , the free energy density of the gel $W(\mathbf{F}, C)$ varies as

$$\delta W = \frac{\partial W}{\partial F_{iK}} \delta F_{iK} + \frac{\partial W}{\partial C} \delta C \quad (5.10)$$

The work done by the external sources is composed of the applied force and the injection of the solvent molecules. The body $\mathbf{B}$ and traction $\mathbf{T}$ forces do work to the system at the rate

$$\int B_i \frac{\delta x_i}{\delta t} dV + \int T_i \frac{\delta x_i}{\delta t} dS \quad (5.11)$$

when the marker of the gel moves to $\mathbf{x}$ at time t at the velocity $\delta x_i / \delta t$.

The injection of the solvent molecules to the system also does work to the system at the rate

$$\int \mu r dV + \int \mu i dS \quad (5.12)$$

Therefore, the total free energy of the thermodynamic system G is the sum of the free energy of the gel, and the potential energy of the force and injection. As such, G changes with time as

$$\frac{\delta G}{\delta t} = \int \frac{\delta W}{\delta t} dV - \int B_i \frac{\delta x_i}{\delta t} dV - \int T_i \frac{\delta x_i}{\delta t} dS - \int \mu r dV - \int \mu i dS \quad (5.13)$$

By substituting Eqs. (5.2), (5.8) and (5.10) into (5.13), and setting $\xi_i = \delta x_i / \delta t$ and $\zeta = \mu$, one obtains

$$\frac{\delta G}{\delta t} = \int \left(\frac{\partial W}{\partial F_{iK}} - P_{iK} \right) \frac{\delta F_{iK}}{\delta t} dV + \int \left(\frac{\partial W}{\partial C} - \mu \right) \frac{\delta C}{\delta t} dV + \int J_K \frac{\partial \mu}{\partial X_K} dV \quad (5.14)$$

Based on the second law of thermodynamics, the free energy of the system never increases, namely,

$$\frac{\delta G}{\delta t} \leq 0 \quad (5.15)$$

The inequality Eqn. (5.15) requires that each integrand in Eqn. (5.14) must either be negative or vanishes. In this theory, the local equilibrium condition of the rearrangement of the molecules is assumed, which leads to the vanishing of the first integrand in Eqn. (5.14), namely

$$P_{iK} = \frac{\partial W(\mathbf{F}, C)}{\partial F_{iK}} \quad (5.16)$$

In addition, the local equilibrium condition is also assumed between the solvent molecules in the gel and those injected. Therefore, the second and third integrands in (5.14) also vanish. As a result,

$$\mu = \frac{\partial W(\mathbf{F}, C)}{\partial C} \quad (5.17)$$

In order to ensure the negative of the free energy rate in Eqn. (5.15), it is commonly to adopt the kinetics of migration for the fourth integrand in Eqn. (5.14),

$$J_K = -M_{KL} \frac{\partial \mu(\mathbf{X}, t)}{\partial X_L} \quad (5.18)$$

where $M_{KL}(\mathbf{F}, C)$ is a mobility tensor which is symmetric and positive-definite.

The nominal J_K and the true j_i fluxes can be converted to each other by

$$j_i = \frac{F_{iK}}{\det(\mathbf{F})} J_K \quad (5.19)$$

Based on the Fickian law, the true flux j_i is defined as

$$j_i = -\frac{cD}{kT} \frac{\partial \mu}{\partial x_i} \quad (5.20)$$

where D is the diffusion coefficient, kT the temperature in the unit of energy. c the true concentration of the solvent, which is related to the nominal concentration as

$$c = \frac{C}{\det(\mathbf{F})} \quad (5.21)$$

Eqs. (5.18) to (5.21) associated with the molecular incompressibility condition (5.9) result in the mobility tensor as

$$M_{KL} = \frac{D}{v k T} H_{iK} H_{iL} [\det(\mathbf{F}) - 1] \quad (5.22)$$

where H_{iK} is the inversion of the deformation gradient $\mathbf{F}$.

The free energy density of the gel $W(\mathbf{F}, C)$ can be the sum of the contributions of the stretching and mixing as (Flory, 1941; Flory, 1953; Flory and Rehner, 1943a, b; Hong *et al.*, 2008; Huggins, 1941)

$$W(\mathbf{F}, C) = \frac{1}{2} N k T [F_{iK} F_{iK} - 2 \log(\det \mathbf{F}) - 3] - \frac{k T}{v} \left[(\det \mathbf{F} - 1) \log \left(\frac{\det \mathbf{F}}{\det \mathbf{F} - 1} \right) + \frac{\chi}{\det \mathbf{F}} \right] \quad (5.23)$$

where N is the number of polymer chains per volume of the gel. χ is a dimensionless parameter characterizing the enthalpy of mixing. It is noted that the molecular incompressibility condition is already imposed on the free energy density equation (5.23). Eqn. (5.23) together with (5.16) and (5.17) constitute the material model in this theory.

5.2.2. Finite Element Model Developed by Zhang *et al.*

Zhang *et al.* (2009) developed a finite element model based on the field theory presented in the last section 5.2.1.

In this finite element model, the displacement $u_i(\mathbf{X}, t)$ and the chemical potential μ are the field variables. The free energy of the gel is thus converted to be a function of deformation gradient $\mathbf{F}$ and chemical potential μ by the Legendre transformation as

$$\begin{aligned} \tilde{W}(\mathbf{F}, \mu) &= W(\mathbf{F}, C) - \mu C \\ &= \frac{1}{2} N k T [F_{iK} F_{iK} - 2 \log(\det \mathbf{F}) - 3] \\ &\quad - \frac{k T}{v} \left[(\det \mathbf{F} - 1) \log \left(\frac{\det \mathbf{F}}{\det \mathbf{F} - 1} \right) + \frac{\chi}{\det \mathbf{F}} \right] - \frac{\mu}{v} (\det \mathbf{F} - 1) \end{aligned} \quad (5.24)$$

The local equilibrium condition can now be expressed as

$$P_{iK} = \frac{\partial \tilde{W}(\mathbf{F}, \mu)}{\partial F_{iK}} \quad (5.25)$$

$$C = -\frac{\partial \tilde{W}(\mathbf{F}, \mu)}{\partial \mu} \quad (5.26)$$

By applying Eqn. (5.25), the weak form of the mechanical equations (5.4)-(5.5) for any test function $\xi_i(\mathbf{X})$ is written as

$$\int \frac{\partial \tilde{W}}{\partial F_{iK}} \frac{\partial \xi_i}{\partial X_K} dV = \int B_i \xi_i dV + \int T_i \xi_i dS \quad (5.27)$$

Similarly, by applying Eqn. (5.26), the weak form of the conservation of solvent molecules (5.6)-(5.7) for any test function $\zeta_i(\mathbf{X})$ is expressed as

$$\begin{aligned} & \int \left(\frac{\partial^2 \tilde{W}}{\partial \mu \partial F_{jL}} \frac{\partial F_{jL}}{\partial t} + \frac{\partial^2 \tilde{W}}{\partial \mu^2} \frac{\partial \mu}{\partial t} \right) \zeta dV - \int M_{KL} \frac{\partial \mu}{\partial X_L} \frac{\partial \zeta}{\partial X_K} dV \\ & = - \int r \zeta dV - \int i \zeta dS \end{aligned} \quad (5.28)$$

The field variables are discretized by the shape function $N_a(\mathbf{X})$ as

$$u_i(\mathbf{X}, t) = x_i(\mathbf{X}, t) - X_i = N_a(\mathbf{X}) u_{ai}(t) \quad (5.29)$$

$$\mu(\mathbf{X}, t) = N_a(\mathbf{X}) \mu_a(t) \quad (5.30)$$

where a is the index of the nodal number. Substituting Eqs. (5.29) and (5.30) into (5.27) and noting the arbitrariness of the test function $\xi_i(\mathbf{X})$, the weak form of mechanical equilibrium equation (5.27) at each node is rewritten as

$$\int \frac{\partial \tilde{W}}{\partial F_{iK}} \frac{\partial N_a}{\partial X_K} dV = \int B_i N_a dV + \int T_i N_a dS \quad (5.31)$$

The above Eqn. (5.31) is valid at any time. Taking the time derivatives, one obtains (Zhang *et al.*, 2009)

$$\begin{aligned} & \frac{du_{bj}}{dt} \int \frac{\partial^2 \tilde{W}}{\partial F_{iK} \partial F_{jL}} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV + \frac{d\mu_b}{dt} \int \frac{\partial^2 \tilde{W}}{\partial F_{iK} \partial \mu} \frac{\partial N_a}{\partial X_K} N_b dV \\ & = \int \frac{dB_i}{dt} N_a dV + \int \frac{dT_i}{dt} N_a dS \end{aligned} \quad (5.32)$$

In a similar way, by substituting Eqs. (5.29) and (5.30) into (5.28), and invoking the arbitrariness of the test function $\zeta(\mathbf{X})$, the weak form of the kinetic equation at each node is given as (Zhang *et al.*, 2009)

$$\begin{aligned}
 & \frac{du_{bj}}{dt} \int \frac{\partial^2 \tilde{W}}{\partial \mu \partial F_{jL}} \frac{\partial N_b}{\partial X_L} N_a dV + \frac{d\mu_b}{dt} \int \frac{\partial^2 \tilde{W}}{\partial \mu^2} N_b N_a dV \\
 & - \mu_b \int M_{KL} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV \\
 & = - \int r N_a dV - \int i N_a dS
 \end{aligned} \tag{5.33}$$

Eqs. (5.32) and (5.33) are of little use for the finite element implementation, since the terms in the integrands are not symmetric. Therefore, the symmetric Green strain tensor $E_{iK}(\mathbf{X}, t)$ and the second Piola-Kirchhoff stress $S_{iK}(\mathbf{X}, t)$ are applied. They are energy conjugated as,

$$S_{iK} = \frac{\partial \tilde{W}}{\partial E_{iK}} \tag{5.34}$$

The Green strain tensor is defined as

$$\begin{aligned}
 E_{iK} &= \frac{1}{2} (C_{iK} - \delta_{iK}) \\
 &= \frac{1}{2} (F_{Li} F_{LK} - \delta_{iK})
 \end{aligned} \tag{5.35}$$

where $C_{iK}(\mathbf{X}, t) = F_{Li} F_{LK}$ is the right Cauchy-Green tensor. By the chain rule, the nominal stress is therefore expressed as

$$P_{iK} = \frac{\partial \tilde{W}}{\partial F_{iK}} = \frac{\partial \tilde{W}}{\partial E_{jL}} \frac{\partial E_{jL}}{\partial F_{iK}} = \frac{\partial \tilde{W}}{\partial E_{KL}} F_{iL} \tag{5.36}$$

The mechanical equation (5.31) at each node is thus rewritten as

$$\int \frac{\partial \tilde{W}}{\partial E_{KL}} F_{iL} \frac{\partial N_a}{\partial X_K} dV = \int B_i N_a dV + \int T_i N_a dS \tag{5.37}$$

Eqs. (5.32) and (5.33) are also rewritten as

$$\begin{aligned}
 & \frac{du_{bj}}{dt} \int \frac{\partial^2 \tilde{W}}{\partial E_{KM} \partial E_{LN}} F_{iM} F_{jN} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV + \frac{d\mu_b}{dt} \int \frac{\partial^2 \tilde{W}}{\partial E_{KM} \partial \mu} F_{iM} \frac{\partial N_a}{\partial X_K} N_b dV \\
 & = \int \frac{dB_i}{dt} N_a dV + \int \frac{dT_i}{dt} N_a dS
 \end{aligned} \tag{5.38}$$

$$\begin{aligned}
 & \frac{du_{bj}}{dt} \int \frac{\partial^2 \tilde{W}}{\partial \mu \partial E_{LM}} F_{jM} \frac{\partial N_b}{\partial X_L} N_a dV + \frac{d\mu_b}{dt} \int \frac{\partial^2 \tilde{W}}{\partial \mu^2} N_b N_a dV \\
 & - \mu_b \int M_{KL} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV = - \int r N_a dV - \int i N_a dS
 \end{aligned} \tag{5.39}$$

Invoking the material model (5.24), the derivative terms in the integrands are expressed as

$$\begin{aligned} \frac{\partial \tilde{W}}{\partial E_{iK}} &= NkT(\delta_{iK} - C_{iK}^{-1}) \\ &\quad - \frac{kT}{v} \left(\det(\mathbf{F}) \ln \frac{\det(\mathbf{F})}{\det(\mathbf{F}) - 1} - 1 - \frac{\chi}{\det(\mathbf{F})} + \frac{\mu}{kT} \det(\mathbf{F}) \right) C_{iK}^{-1} \end{aligned} \quad (5.40)$$

$$\begin{aligned} \frac{\partial \tilde{W}}{\partial E_{iK} \partial E_{jL}} &= NkT \left(C_{ij}^{-1} C_{KL}^{-1} + C_{iL}^{-1} C_{Kj}^{-1} \right) \\ &\quad + \frac{kT}{v} \left(\det(\mathbf{F}) \ln \frac{\det(\mathbf{F})}{\det(\mathbf{F}) - 1} - 1 - \frac{\chi}{\det(\mathbf{F})} + \frac{\mu}{kT} \det(\mathbf{F}) \right) \left(C_{ij}^{-1} C_{KL}^{-1} + C_{iL}^{-1} C_{Kj}^{-1} \right) \\ &\quad - \frac{kT}{v} \left(\det(\mathbf{F}) \ln \frac{\det(\mathbf{F})}{\det(\mathbf{F}) - 1} - \frac{\det(\mathbf{F})}{\det(\mathbf{F}) - 1} + \frac{\chi}{\det(\mathbf{F})} + \frac{\mu}{kT} \det(\mathbf{F}) \right) C_{jL}^{-1} C_{iK}^{-1} \end{aligned} \quad (5.41)$$

$$\frac{\partial^2 \tilde{W}}{\partial E_{iK} \partial \mu} = - \frac{\det(\mathbf{F}) C_{iK}^{-1}}{v} \quad (5.42)$$

$$\frac{\partial^2 \tilde{W}}{\partial \mu^2} = 0 \quad (5.43)$$

where $C_{iK}^{-1}(\mathbf{X}, t)$ is the inversion of the right Cauchy-Green tensor $C_{iK}(\mathbf{X}, t)$, and the following relations are applied,

$$\frac{\partial \det(\mathbf{F})}{\partial E_{iK}} = \det(\mathbf{F}) C_{iK}^{-1} \quad (5.44)$$

$$\frac{\partial C_{iK}^{-1}}{\partial E_{jL}} = - \left(C_{ij}^{-1} C_{KL}^{-1} + C_{Kj}^{-1} C_{iL}^{-1} \right) \quad (5.45)$$

Eqs. (5.38) and (5.39) are the ordinary differential equations with the two unknowns, the displacement $u_{bj}(t)$ and chemical potential $\mu_b(t)$. They can be rewritten in a matrix form as

$$\mathbf{L} \frac{d\mathbf{w}}{dt} + \mathbf{K} \mathbf{w} = \mathbf{R} \quad (5.46)$$

where the vector $\mathbf{w}$ lists the values of $u_{bj}(t)$ and $\mu_b(t)$ at all the nodes. The matrix $\mathbf{L}$ collects the integrals involving the second derivatives of the free energy function, and the matrix $\mathbf{K}$ collects the integral involving the mobility tensor.

The ordinary differential equation (5.46) can be discretized in time domain by implicit method, where the increment of the nodal value $\Delta \mathbf{w}$ at time $t + \Delta t$ is obtained by

$$\mathbf{A}^{t+\Delta t} \Delta \mathbf{w} = \mathbf{Y}^{t+\Delta t} \quad (5.47)$$

and

$$\mathbf{A}^{t+\Delta t} = \frac{\mathbf{L}^{t+\Delta t}}{\Delta t} + \mathbf{K}^{t+\Delta t} \quad (5.48)$$

$$\mathbf{Y}^{t+\Delta t} = \mathbf{R}^{t+\Delta t} - \mathbf{L}^t \frac{d\mathbf{w}^t}{dt} - \mathbf{K}^t \mathbf{w}^t \quad (5.49)$$

One of the methods to solve Eqn. (5.47) is the direct solver, where the matrix $\mathbf{A}$ is required to be positive definite. However, the matrix $\mathbf{A}$ here is indefinite since the positive definite mobility tensor contributes to the negative of the matrix. Moreover, when the material instability occurs, the matrix $\mathbf{A}$ may be singular (Zhang *et al.*, 2009). In order to overcome these problems, a simple shifting method is implemented by replacing matrix $\mathbf{A}$ with (Zhang *et al.*, 2009)

$$\mathbf{A}^* = \mathbf{A} + \lambda \mathbf{I} \quad (5.50)$$

where λ is a positive number as a penalty to ensure the positive definiteness of the stiffness matrix $\mathbf{A}^*$ (Zhang *et al.*, 2009). This method is widely used in finite element analysis, especially in eigenproblems (Bathe, 2005).

The above finite element model is implemented in the ABAQUS/standard software via the USER-ELEMENT subroutine (UEL), by formulating the stiffness matrix and loading vector at each element.

5.2.3. Case Studies by Simulation and Experiment

In this subsection, we analyze various deformations of the gel in a solvent via the above finite element model and experiments, respectively.

In order to implement the finite element model, the function of free energy density and the stress are normalized by kT/v , and the chemical potential by kT . The time is normalized by the characteristic length L and the diffusion coefficient D , i.e., L^2/D . The representative value of the volume of per molecule is $v = 10^{-28} \text{ m}^3$, and thus $kT = 4 \times 10^{-21} \text{ J}$ and $kT/v = 4 \times 10^7 \text{ Pa}$ at room temperature. The normalization leads to two dimensionless material parameters, namely Nv and χ . Usually they are in the range of $Nv = 10^{-4} \sim 10^{-1}$ and $\chi = 0 \sim 1.2$. In the numerical examples below, $Nv = 10^{-3}$ and $\chi = 0.2$ are taken, and the diffusion coefficient is $D = 8 \times 10^{-10} \text{ m}^2/\text{s}$ (Hong *et al.*, 2008).

5.2.3.1 Swelling of Constrained Gel

Let us consider the two constrained gels in this subsection. The first is a gel for fluidic control in 1-D domain, as shown in Fig. 5.2, where the gel is pre-stretched and confined in the lateral directions (i.e., X_2 and X_3) and is allowed to swell in the X_1 direction only. In Fig. 5.2, the swelling or shrinking of the gel pushes or pulls the piston to open or close the valves, and thus to control the fluid flow through different routines, where the permeable rigid plates allow the fluid molecules to migrate from the environment to gel or vice versa. The constrained gel in Fig. 5.2 can be simplified to a 1-D problem analytically, where the stretch λ_1 in the X_1 direction and the chemical potential μ are governed as (Hong *et al.*, 2008),

$$\frac{\partial \lambda_1}{\partial t} = D \frac{\partial}{\partial X_1} \left[\left(1 - \frac{1}{\lambda_2^2 \lambda_1} \right) \left(\frac{1}{(\lambda_2^2 \lambda_1 - 1) \lambda_2^2 \lambda_1^3} - \frac{2\chi}{\lambda_2^4 \lambda_1^4} + \frac{Nv}{\lambda_2^2 \lambda_1} \left(1 + \frac{1}{\lambda_1^2} \right) \right) \frac{\partial \lambda_1}{\partial X_1} \right] \quad (5.51)$$

$$\mu = Nv \left(\lambda_1 - \frac{1}{\lambda_1} \right) + \lambda_1^2 \log \left(1 - \frac{1}{\lambda_1 \lambda_3^2} \right) + \frac{1}{\lambda_1} + \frac{\chi}{\lambda_1^2 \lambda_3^2} \quad (5.52)$$

with the boundary conditions

$$\left[Nv \left(\lambda_1 - \frac{1}{\lambda_1} \right) + \lambda_1^2 \log \left(1 - \frac{1}{\lambda_1 \lambda_3^2} \right) + \frac{1}{\lambda_1} + \frac{\chi}{\lambda_1^2 \lambda_3^2} \right]_{X_1=L} = 0 \quad (5.53)$$

$$\left. \frac{\partial \lambda_1}{\partial X_1} \right|_{X_1=0} = 0 \quad (5.54)$$

and the initial condition

$$\lambda_1(X_1, 0) = 1 \quad (5.55)$$

The pre-stretching ratios in the lateral directions are assumed to be $\lambda_2 = \lambda_3 = 4.0$.

In this subsection, the finite element model described in Section 5.2.2 is used for simulation of the above gel by the 40 eight-node brick elements, where the surfaces of the gel constrained by the permeable rigid plates are prescribed by the vanishing displacement and flux, and the free surface contacted directly with the piston is prescribed by the vanishing chemical potential.

Fig. 5.3 presents the stretch ratio λ_1 and the normalized chemical potential $\bar{\mu}$ evolving with time, where the discrete markers are the finite element results and the

continuous lines the results from the finite difference method. It is seen from Fig. 5.3 that initially, the gel is in the state with small fluid content, and thus the chemical potential is negative. As such, the stretch ratio remains unchanged since the water has no time to diffuse into the network. With time evolution however, the fluid content increases in the networks, and the gel swells, stretches and reaches the boundary value. Correspondingly, the chemical potential approaches zero. The results obtained by the present finite element model are compared with the finite-difference solutions, and they agreed well as shown in Fig. 5.3.

The second constrained gel is a sheet of gel clamped on the bottom face and constrained in the thickness direction, as shown in Fig. 5.4(a), where the gel sheet is allowed to swell in the other two directions only. In other words, the gel sheet with the fixed thickness is a quasi-2D problem, which has also been analyzed experimentally (Achilleos *et al.*, 2000). In the present finite element analysis, the gel is modeled by 882 eight-node brick elements, where the free surfaces in direct contact with the water are prescribed by vanishing chemical potential, and the clamped bottom surface by vanishing displacement and flux, and the constrained surfaces are prescribed by vanishing displacement and flux in thickness direction. Figs. 5.4(b)-(e) illustrate the water content in the gel with time evolution, where the gel swells faster at the corner than at the center at initially short time (e.g., $Dt / L^2 = 0.7, 10$), and thus the deformation is inhomogeneous, as shown in Figs. 5.4(b)-(c). Meanwhile, the water has no time to migrate to the center and thus accumulates around the surfaces of the gel, the chemical potential then decreases gradually from the corner and edge to the center. As time goes on, the swelling at the center catches up with that at the corners and edges, and thus the curvature of the edges becomes less concave. Consequently, the chemical potential also approaches to zero, as shown in Figs. 5.4(d)-(e). Finally, the gel is fully saturated with the water and the chemical potential approach zero throughout the gel, when the swelling reaches equilibrium. The same swelling process for the gel sheet was also observed in the experiment (Achilleos *et al.*, 2000), where the polymer content was shown.

5.2.3.2 Free Swelling of Block Gel

The gels with different geometric shapes in water may develop different deformation patterns. In this subsection, free swelling of different block gels in water,

including the cubic, cylindrical and spherical gels, is investigated in details by the present finite element model and experiment.

The cubic gel in the water may develop wrinkles during the swelling. In order to understand the wrinkling pattern, we conduct the experiment and the simulation in this subsection. In the present experiment, we use a $4.5 \times 4.5 \times 4.5\text{mm}$ dry cubic gel that is immersed in water and is allowed to swell freely, where the original dry state of the gel is shown in Fig. 5.5(a). After being immersed in water, wrinkles developed on the edges, as observed in Fig. 5.5(b) at time $t = 4\text{ min}$, where the waves are formed along the edges. After several hours, the gel reaches the equilibrium state with water, where it recovers the original geometric shape but possesses much larger volume, as observed in Fig. 5.5(c). In the finite element simulation, the length L of the cubic gel is applied to normalize the time. Due to the symmetry of the present deformation, only one-eighth of the cubic gel is modeled by 512 brick elements, where the vanishing displacement and flux are prescribed on the symmetric faces, and the vanishing chemical potential is imposed on the free surfaces. Fig. 5.6 plots the stress contours by the finite element simulation. The simulation predicts the wrinkles well as shown in Fig. 5.6(b), where the compressive stress occurs within the interior surfaces and the tensile stress on the waves along the edge surfaces. It is demonstrated that the buckling patterns may be induced by the different stress states. The surfaces around the edges of the cube swell much faster due to sufficient contact with the environmental water. The finite element simulation is also able to predict that the cubic gel finally recovers the original geometric shape at equilibrium state, but has a much larger volume as shown in Fig. 5.6(c), in which the stress vanishes. The cubic gel was also simulated by Zhang *et al.* (2009), where the bowl-like surface was achieved during the swelling. In the present simulation however, it is shown that the wrinkles are developed during the swelling, which are validated by the above experiments.

The free swelling of a cylindrical gel in the water is presented in Fig. 5.7. In this simulation, the time is nondimensionalized by the diffusion coefficient D and the height of the gel H . The dry state of the gel is stress-free, as shown in Fig. 5.7(a). After immersed into the water, the gel starts to swell as observed in Figs. 5.7(b) and (c), where the relative faster swelling on the edges generates the compressive stress inside the gel, and thus the gel wrinkles. With time evolution, the swelling inside the gel catches up with that along the edges and wrinkles thus reduce, as shown in Fig. 5.7(d). Finally, the gel becomes homogeneously deformed with stress-free state, and

the gel also recovers the original geometry but has much larger volume, as shown in Fig. 5.7(e). The similar swelling process was also observed in experiments (Sayil and Okay, 2001), where the wrinkling patterns and the shape recovering phenomena were found.

For the spherical gel immersed into the water, Fig. 5.8 illustrates the chemical potential during the swelling, where the radius of the spherical gel R is applied to normalize the time in the simulation. At the dry state (i.e., $Dt / R^2 = 0$), no water exists in the gel, as shown in Fig. 5.8(a). When the gel is immersed into the water, the chemical potential of the pure water is set to be zero, and thus the chemical potential over the interface is also zero between the gel and the water, since the surfaces of the gel are assumed to be saturated immediately. Relatively, the chemical potential of the unsaturated part in the gel thus is negative. At time $Dt / R^2 = 12.5$, the gel swells and the water content inside the gel increases from the surface to the center gradually, as shown in Fig. 5.8(b). Finally, at equilibrium state, the whole gel is fully saturated by the water and the chemical potential is zero all over the gel, as observed in Fig. 5.8(c).

5.2.3.3 Free Swelling of Thin Film of Gel

In this subsection, the various thin films of the gels immersed into the water are studied via the finite element model and experiment. They include the thin plate, the thin disk, and the spherical shell of the gels.

As the first example of the thin film of the gel, a thin plate of gel immersed in water without any constraint is studied by both the experiment and simulation. In the present experiment, we use a dry gel plate with the dimensions of $7 \times 4 \times 1\text{mm}$, as shown in Fig. 5.9(a). After the gel is placed in water, it quickly develops wrinkles at the edges, which become wavy, as observed in Fig. 5.9(b). After several hours, the gel reaches equilibrium and recovers its original geometric shape but has much larger volume, as shown in Fig. 5.9(c). In the simulation, the plate width w is used to normalize the time. Due to the symmetry of the plate deformation, only one-eighth of the plate is implemented in the simulation, where the symmetric faces are prescribed by vanishing flux and displacement, and the other surfaces by vanishing chemical potential. At time $Dt / w^2 = 1$, the wrinkles are found as shown in Fig. 5.10(b), where the contours plots demonstrate that the stresses are negative on the central

portion of the top and bottom surfaces, and thus the compressive stress induces the buckling on the edges. The simulation buckling pattern shown in Fig. 5.10(b) agrees well with the present experiments shown in Fig. 5.9(b). After the thin plate of gel reaches equilibrium, the stress vanishes all over the gel as seen in Fig. 5.10(c), where the gel recovers the original geometric shape but has much larger volume. This also coincides with the present experimental observation in Fig. 5.9(c).

As the second example of the thin film of the gel, the free swelling of a thin disk of gel is demonstrated in Fig. 5.11, where the radius of the disk gel R is applied to nondimensionalize the time. As illustrated in the figure, the compressive stress is developed on the surface of the disk gel during the swelling, which leads to wrinkles on the edges. Meanwhile, the tensile stress inside the gel expands itself to contain the solvent molecules diffused from environment. Finally, the disk gel at equilibrium recovers its original geometry but has much larger volume.

As the last example of the thin film of the gel, the free swelling of a spherical shell of gel in the water is presented in Fig. 5.12, where the time is normalized by the thickness of the shell h . As observed in Fig. 5.12(b), the buckling is developed in short time, since the compressive stress exists on the outer surface and the tensile stress on the inner surface at $Dt / h^2 = 10$. However, the deformation of the shell becomes increasingly homogeneous after long time at $Dt / h^2 = 100$, and the stress converges to zero with the swelling as shown in Fig. 5.12(c). Finally, the gel becomes homogeneous deformation with stress-free state, and the gel recovers its original geometry but occupies a much larger volume at equilibrium, as shown in Fig. 5.12(d).

5.2.3.4 Swelling of Bonded Gel

In this subsection, the kinetic swelling of the strip gel with different constraint conditions in water is investigated, since the kinetics is of importance in applications of gel. The various constraints may induce different deformation patterns, for example, wrinkling, twisting, folding, waving and buckling. In the present simulation, the four kinds of constraints are imposed on the strip gels. The first is to fix the both ends of a long straight strip gel as shown in Fig. 5.13(a); the second to fix a single long edge of a straight strip gel as shown in Fig. 5.14(a); the third to fix a single surface of a straight strip gel as shown in Fig. 5.15(a); and the last to fix the inner circular edge of a circular strip gel as shown in Fig. 5.16(a). Here the free surfaces that are contacted

directly with water are prescribed by vanishing chemical potential, while the surfaces with constraints by vanishing displacement and flux. The time is normalized by the thickness h of the gel strip and the diffusivity D .

For the first constraint case via fixing the both ends of a long straight strip gel, Fig. 5.13 illustrates the kinetics of the strip gel in the water, where the geometry and constraints of the gel are shown in Fig. 5.13(a). In this simulation, only half of the strip is modeled due to the symmetry. The gel strip starts to twist at time $Dt / h^2 = 1.8$ as observed in Fig. 5.13(b), where the twisting is due to the buckling with large wavelength, since the different stress states result from the fast swelling at the corners and edges. As time goes on, the gel strip slowly folds itself as shown in Fig. 5.13(c)-(e), where the compressive stress around the wave crest and through the tensile stress between them induce the folding more compact. At the equilibrium state, the strip fully folds itself as observed in Fig. 5.13(f), where the stress almost vanishes all around the gel but exists near the constraints. The folding behavior of the strip was also observed in experiments by Singamaneni *et al.* (2010), which is comparable with the present simulation results.

For the second constraint case via fixing a single long edge of a straight strip gel, Fig. 5.14 plots the swelling of the strip gel in the water, where the geometry and constraints of the gel are shown in Fig. 5.14(a). After immersed into water, the gel becomes wavy as seen in Figs. 5.14(b)-(c), where the waves become more compact and the thickness of the gel increases with time. Finally, when the gel reaches the equilibrium state, it fully swells and the waves almost disappear. The simulation achieves the similar deformation pattern to that in the experiment by Mora and Boudaoud (2006).

For the third constraint case via fixing a single surface of a straight strip gel, Fig. 5.15 presents the swelling of the strip gel in the water, where the geometry and constraints of the gel are shown in Fig. 5.15(a). Initially, the wrinkles are developed due to the faster swelling on the corners and edges at $Dt / h^2 = 10$, as shown in Fig. 5.15(b). With time evolution, the wrinkles become smoother and finally disappear at equilibrium as shown in Figs. 5.15(c)-(d). Due to the constraints on the bottom surface, the fully swollen gel can no longer recover its original geometric shape.

For the last constraint case via fixing the inner circular edge of a circular strip gel, Fig. 5.16 shows the buckling pattern of the circular strip gel in the water, where the

origin geometric shape of the gel is illustrated in Fig. 5.16(a), and the buckling waves at equilibrium state in Fig. 5.16(b). In the simulation, the inner r and outer R radii are applied to normalize the time, where the gel is clamped along the inner edge surface and the other surfaces can deform freely. The wavy pattern is in good agreement with the experimental observation (Mora and Boudaoud, 2006). Finally, the maximum stress on the inner edge after equilibrium is also coincidence with the experiment observation (Mora and Boudaoud, 2006).

5.3. Steady-State Analysis of Dielectrics

Dielectrics, also know as dielectric gel, is a kind of smart materials whose mechanical properties may be altered by imposing an electric field and/or mechanical load. Dielectric gels can undergo large deformation under a voltage, due to the electrostatic pressure arising from the Coulomb force between electrodes.

In this section, based on the field theory (Suo *et al.*, 2008), we develop a finite element formulation for analysis of the dielectrics, it is followed by the two case studies. The first is to analyze dielectrics subjected to an electromechanical load, and the second to simulate the dielectrics within the solvent under a voltage.

5.3.1. Field Theory Proposed by Suo et al.

Suo *et al.* (2008) proposed a field theory for the deformation of dielectric gel, in which the dielectric gel deforms when applied the voltage by the batteries and force via the weights, since the voltage and the weights do work to the gel. Therefore, the gel, the batteries and the weights form a thermodynamic system. The theory is composed of two field equations, namely the charge and the mechanical equilibrium equations, in order to couple the electric field with large deformation for the system under the stimuli of the electric potential and external force.

In this theory, the deformation gradient $\mathbf{F}$ and the nominal stress $\mathbf{P}$ are defined in a same manner as Eqs. (5.1) and (5.2) in the Section 5.2. The field equations of mechanical equilibrium (5.4) and (5.5) are thus rewritten again as

$$\frac{\partial P_{iK}(\mathbf{X}, t)}{\partial X_K} + B_i(\mathbf{X}, t) = 0 \quad (5.56)$$

$$P_{iK}(\mathbf{X}, t) N_K(\mathbf{X}, t) = T_i(\mathbf{X}, t) \quad (5.57)$$

If $\psi(\mathbf{X}, t)$ represents the electric potential, the nominal electric field $\tilde{E}_K^f(\mathbf{X}, t)$ is defined as

$$\tilde{E}_K^f(\mathbf{X}, t) = -\frac{\partial \psi(\mathbf{X}, t)}{\partial X_K} \quad (5.58)$$

In the current state, the charge in a control volume is denoted as $Q(\mathbf{X}, t)dV(\mathbf{X})$, and the charge on the surface of the volume as $\Omega(\mathbf{X}, t)dS(\mathbf{X})$. For any test function $\zeta(\mathbf{X})$, the nominal electric displacement $\tilde{D}_K(\mathbf{X}, t)$ is defined as

$$-\int \frac{\partial \zeta}{\partial X_K} \tilde{D}_K dV = \int Q \zeta dV + \int \Omega \zeta dS \quad (5.59)$$

Applying the divergence theorem to Eqn. (5.59), the field equation for the electric equilibrium is obtained as

$$\frac{\partial \tilde{D}_K(\mathbf{X}, t)}{\partial X_K} = Q(\mathbf{X}, t) \quad (\text{In the volume}) \quad (5.60)$$

$$\tilde{D}_K(\mathbf{X}, t)N_K(\mathbf{X}, t) = \Omega(\mathbf{X}, t) \quad (\text{On the surface}) \quad (5.61)$$

The free energy density of the dielectric gel $W(\mathbf{F}, \tilde{\mathbf{D}})$ is defined as a function of the deformation gradient $\mathbf{F}$ and the electric displacement $\tilde{\mathbf{D}}$. With the small changes of $\delta \mathbf{F}$ and $\delta \tilde{\mathbf{D}}$, the free energy density varies as

$$\delta W = \frac{\partial W}{\partial F_{iK}} \delta F_{iK} + \frac{\partial W}{\partial \tilde{D}_K} \delta \tilde{D}_K \quad (5.62)$$

The work done by the body $\mathbf{B}$ and traction $\mathbf{T}$ forces due to the small variation of displacement δx_i is given as

$$\int B_i \delta x_i dV + \int T_i \delta x_i dS \quad (5.63)$$

The small change of charges also does work to the system by

$$\int \psi \delta Q dV + \int \psi \delta \Omega dS \quad (5.64)$$

The variation of the total free energy of the thermodynamic system is thus given as

$$\delta G = \int \delta W dV - \int B_i \delta x_i dV - \int T_i \delta x_i dS - \int \psi \delta Q dV - \int \psi \delta \Omega dS \quad (5.65)$$

Applying Eqs. (5.2) and (5.59) to (5.65), and invoking $\zeta = \psi$ and $\xi_i = x_i$, one obtains

$$\delta G = \int \left(\frac{\partial W}{\partial F_{iK}} - P_{iK} \right) \delta F_{iK} dV + \int \left(\frac{\partial W}{\partial \tilde{D}_K} - \tilde{E}_K^f \right) \delta \tilde{D}_K dV \quad (5.66)$$

The thermodynamics requires $\delta G = 0$ at an equilibrium state for any small change of deformation gradient $\mathbf{F}$ and electric displacement $\tilde{\mathbf{D}}$, leading to

$$P_{iK} = \frac{\partial W(\mathbf{F}, \tilde{\mathbf{D}})}{\partial F_{iK}} \quad (5.67)$$

$$\tilde{E}_K = \frac{\partial W(\mathbf{F}, \tilde{\mathbf{D}})}{\partial \tilde{D}_K} \quad (5.68)$$

Once the function of the free energy density $W(\mathbf{F}, \tilde{\mathbf{D}})$ is specified, the theory can be solved analytically or numerically.

5.3.2. Development of Finite Element Model

In this subsection, we develop the finite element formulation for the dielectric gels, based on the field theory presented in the subsection 5.3.1.

In order to formulate the finite element model, the free energy density is transformed as a function of deformation gradient $\mathbf{F}$ and nominal electric field $\tilde{\mathbf{E}}$ by the Legendre method,

$$\tilde{W}(\mathbf{F}, \tilde{\mathbf{E}}) = W - \tilde{E}_K^f \tilde{D}_K \quad (5.69)$$

Consequently, Eqs. (5.67) and (5.68) can be rewritten as

$$P_{iK} = \frac{\partial \tilde{W}(\mathbf{F}, \tilde{\mathbf{E}}^f)}{\partial F_{iK}} \quad (5.70)$$

$$\tilde{D}_K = - \frac{\partial \tilde{W}(\mathbf{F}, \tilde{\mathbf{E}}^f)}{\partial \tilde{E}_K^f} \quad (5.71)$$

Interpolating the field variables u_i and ψ by shape function $N_a(\mathbf{X})$ leads to

$$u_i(\mathbf{X}) = u_{ai} N_a(\mathbf{X}) \quad (5.72)$$

$$\psi(\mathbf{X}) = \psi_a N_a(\mathbf{X}) \quad (5.73)$$

The weak forms of the two field equations in the finite element formulation are thus expressed as

$$\int \frac{\partial \tilde{W}}{\partial F_{iK}} \frac{\partial N_a}{\partial X_K} dV = \int B_i N_a dV + \int T_i N_a dS \quad (5.74)$$

$$\int \frac{\partial \tilde{W}}{\partial \tilde{E}_K^f} \frac{\partial N_a}{\partial X_K} dV = \int N_a Q dV + \int N_a \Omega dA \quad (5.75)$$

The above two nonlinear field equations (5.74) and (5.75) could be solved by Newton-Raphson method, and the increments of the nodal variables Δu_{bj} and $\Delta \psi_b$ for each time step are given as

$$\begin{aligned} & \Delta u_{bj} \int \frac{\partial^2 \tilde{W}}{\partial F_{iK} \partial F_{jL}} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV - \Delta \psi_b \int \frac{\partial^2 \tilde{W}}{\partial F_{iK} \partial \tilde{E}_L^f} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV \\ &= \int B_i N_a dV + \int T_i N_a dS - \int \frac{\partial \tilde{W}}{\partial F_{iK}} \frac{\partial N_a}{\partial X_K} dV \end{aligned} \quad (5.76)$$

$$\begin{aligned} & -\Delta \psi_b \int \frac{\partial^2 \tilde{W}}{\partial \tilde{E}_K^f \partial \tilde{E}_L^f} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV + \Delta u_{bj} \int \frac{\partial^2 \tilde{W}}{\partial \tilde{E}_K^f \partial F_{jL}} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV \\ &= \int N_a Q dV + \int N_a \Omega dA - \int \frac{\partial \tilde{W}}{\partial \tilde{E}_K^f} \frac{\partial N_a}{\partial X_K} dV \end{aligned} \quad (5.77)$$

By applying the same symmetric strategy as that in Section 5.2.2, the symmetric forms of Eqs. (5.76) and (5.77) are expressed as

$$\begin{aligned} & \Delta u_{bj} \int \frac{\partial^2 \tilde{W}}{\partial E_{KM} \partial E_{LN}} F_{iM} F_{jN} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV \\ & - \Delta \psi_b \int \frac{\partial^2 \tilde{W}}{\partial E_{KM} \partial \tilde{E}_L^f} F_{iM} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV \\ &= \int B_i N_a dV + \int T_i N_a dS - \int \frac{\partial \tilde{W}}{\partial F_{iK}} \frac{\partial N_a}{\partial X_K} dV \end{aligned} \quad (5.78)$$

$$\begin{aligned} & -\Delta \psi_b \int \frac{\partial^2 \tilde{W}}{\partial \tilde{E}_K^f \partial \tilde{E}_L^f} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV + \Delta u_{bj} \int \frac{\partial^2 \tilde{W}}{\partial \tilde{E}_K^f \partial E_{KM}} F_{iM} \frac{\partial N_a}{\partial X_K} \frac{\partial N_b}{\partial X_L} dV \\ &= \int N_a Q dV + \int N_a \Omega dA - \int \frac{\partial \tilde{W}}{\partial \tilde{E}_K^f} \frac{\partial N_a}{\partial X_K} dV \end{aligned} \quad (5.79)$$

After integration, the above Eqs. (5.78) and (5.79) become ordinary differential equations, where the specified material law is required to implement to the USER-ELEMENT subroutine UEL of the commercial software ABAQUS/standard.

5.3.3. Case Studies by Simulation

In this subsection, we conduct two case studies of the dielectric gels subject to electromechanical loads without and within solvent, where these two different environmental conditions impose the different functions of free energy density.

5.3.3.1 Dielectrics Subject to Electromechanical Load

In this subsection, the first case study is carried out for the dielectric gels subject to electromechanical load without solvent, through two examples of the dielectric gels without and with mechanical load, respectively.

In general, the dielectrics can undergo large shape change without appreciable volumetric change (Zhao and Suo, 2007). It is therefore reasonable to assume the condition of incompressibility as

$$\det \mathbf{F} = 1 \quad (5.80)$$

The free energy density of the dielectrics is due to stretching and polarizing, which can be expressed as (Zhao *et al.*, 2007)

$$\tilde{W} = \frac{\eta}{2} [C_{KK} - 2 \ln(\det \mathbf{F}) - 3] - \frac{\varepsilon \tilde{E}_K C_{KL}^{-1} \tilde{E}_L}{2 \det \mathbf{F}} + \Pi (\det \mathbf{F} - 1)^2 \quad (5.81)$$

where η is the shear modulus, and Π is a number much greater than η to enforce the incompressibility of the dielectrics. The derivatives in Eqs. (5.78) and (5.79) can thus be written as

$$\begin{aligned} \frac{\partial \tilde{W}}{\partial E_{iK}} &= \eta (\delta_{iK} - C_{iK}^{-1}) - \frac{1}{2} \varepsilon \sqrt{I_3} \tilde{E}_M^f \tilde{E}_N^f [C_{iK}^{-1} C_{MN}^{-1} - 2 C_{iM}^{-1} C_{NK}^{-1}] \\ &\quad + 2 \Pi (\det \mathbf{F} - 1) \det \mathbf{F} C_{iK}^{-1} \end{aligned} \quad (5.82)$$

$$\frac{\partial \tilde{W}}{\partial \tilde{E}_i^f} = -\varepsilon \det \mathbf{F} C_{iK}^{-1} \tilde{E}_K^f \quad (5.83)$$

$$\begin{aligned} &\frac{\partial^2 \tilde{W}}{\partial E_{iK} \partial E_{jL}} \\ &= \eta (C_{ij}^{-1} C_{KL}^{-1} + C_{Kj}^{-1} C_{iL}^{-1}) - \frac{1}{2} \varepsilon \sqrt{I_3} C_{jL}^{-1} \tilde{E}_M^f \tilde{E}_N^f (C_{iK}^{-1} C_{MN}^{-1} - 2 C_{Mi}^{-1} C_{NK}^{-1}) \\ &\quad + \frac{1}{2} \varepsilon \sqrt{I_3} \tilde{E}_M^f \tilde{E}_N^f [C_{MN}^{-1} (C_{ij}^{-1} C_{KL}^{-1} + C_{Kj}^{-1} C_{iL}^{-1}) + 2 C_{iK}^{-1} (C_{Mj}^{-1} C_{NL}^{-1})] \\ &\quad - \frac{1}{2} \varepsilon \sqrt{I_3} \tilde{E}_M^f \tilde{E}_N^f [2 C_{Mi}^{-1} (C_{Nj}^{-1} C_{KL}^{-1} + C_{NL}^{-1} C_{Kj}^{-1}) + 2 C_{NK}^{-1} (C_{Mj}^{-1} C_{Li}^{-1} + C_{ML}^{-1} C_{ij}^{-1})] \\ &\quad + 2 \Pi (2 \det \mathbf{F} - 1) \det \mathbf{F} C_{iK}^{-1} C_{jL}^{-1} - 2 \Pi (\det \mathbf{F} - 1) \det \mathbf{F} (C_{ij}^{-1} C_{KL}^{-1} + C_{Kj}^{-1} C_{iL}^{-1}) \end{aligned} \quad (5.84)$$

$$\frac{\partial^2 \tilde{W}}{\partial \tilde{E}_i^f \partial E_{jL}} = -\varepsilon \tilde{E}_K^f \det \mathbf{F} [C_{jL}^{-1} C_{iK}^{-1} - (C_{ij}^{-1} C_{KL}^{-1} + C_{iL}^{-1} C_{Kj}^{-1})] \quad (5.85)$$

$$\frac{\partial^2 \tilde{W}}{\partial \tilde{E}_K^f \partial \tilde{E}_L^f} = -\varepsilon \det \mathbf{F} C_{KL}^{-1} \quad (5.86)$$

The field equations (5.78) and (5.79) as well as (5.82) to (5.86) are solved by the

UEL in ABAQUS/standard to simulate the dielectrics under the voltage and the mechanical load. In the finite element formulation, the nominal electric field $\tilde{E}^f$, the nominal stress P , and displacement $\tilde{D}$ are normalized as

$$\bar{E} = \tilde{E}^f \sqrt{\varepsilon / \eta}, \quad \bar{P} = \frac{P}{\eta}, \quad \bar{D} = \frac{\tilde{D}}{\sqrt{\varepsilon \eta}} \quad (5.87)$$

As the first example of the dielectric gels without mechanical load, a flat layer of dielectrics covered by electrodes on both surfaces is analyzed, as shown in Fig. 5.17(a), where the initial thickness of the layer is L , the deformed thickness λL , and λ the stretching ratio. The analytical solution of the relationship between the electric field $\bar{E}$ and stretching ratio λ is given as (Zhao *et al.*, 2007),

$$\bar{E} = \sqrt{\lambda - \lambda^4} \quad (5.88)$$

where the electric field $\bar{E}$ thins down the dielectrics to minimize the free energy of the system. Fig. 5.17(b) shows the finite element results represented by circles and the analytical solution by line. The above FEM code is able to exactly reproduce the thinning behavior of the dielectrics under a voltage.

As the second example of the dielectric gels with mechanical load, a flat layer of dielectrics under different mechanical loads and voltages is investigated by the finite element formulation, as shown in Fig. 5.18, where the biaxial loads $P_1 / \eta = P_2 / \eta = P / \eta$ are applied to the dielectrics, and thus the stretches become $\lambda_1 = \lambda_2 = \lambda$. The behavior is given analytically by Zhao and Suo (2007), where the relations between λ , $\bar{D}$ and $\bar{E}$ are given as

$$\bar{D} = \sqrt{\lambda^6 - 1 - \frac{P}{\eta} \lambda^5}, \quad \bar{E} = \sqrt{\lambda^{-2} - \lambda^{-8} - \frac{P}{\eta} \lambda^{-3}} \quad (5.89)$$

The biaxial loads result in a pre-stretches λ_p , the total stretching is thus normalized by the pre-stretch λ / λ_p . Fig. 5.19 illustrates both the FEM results and analytical solutions for the electric field $\bar{E}$ as a function of biaxial stretches λ . It is observed from Fig. 5.19 that the electric field $\bar{E}$ increases with the increase of the load P / η . The larger the load P / η is, the larger the increment of the electric field $\bar{E}$ is. Fig. 5.20 plots the electric displacement $\bar{D}$ as a function of the pre-stress P / η and the biaxial stretches λ for both the analytical and FEM solutions. It is found in Fig. 5.20 that the electric displacement $\bar{D}$ increases with the increase of the

pre-stress P / η and stretch λ in order to minimize the free energy of the system. In brief, the FEM can capture the behavior of the dielectrics quite accurately.

5.3.3.2 Dielectrics in Solvent

In this subsection, the second case study is carried out for the dielectric gels subject to electromechanical load within solvent, through two examples of the dielectric gels with and without constraints, respectively.

The behavior of the dielectric gel immersed in the solvent and subject to electromechanical load is studied in this subsection, as shown in Fig. 5.21, by the finite element formulation developed in the subsection 5.3.2. Since the gel is immersed into the solvent, it may imbibe solvent molecules into the network, and the free energy of the gel results from the interaction between the polymer chains and the solvent molecules. For an ideal dielectric gel, the free energy density could be specified as (Zhao *et al.*, 2008)

$$\begin{aligned} \tilde{W}(\mathbf{F}, \tilde{\mathbf{E}}) = & \frac{1}{2} NkT [F_{iK} F_{iK} - 2 \log(\det \mathbf{F}) - 3] \\ & - \frac{kT}{v} \left[(\det \mathbf{F} - 1) \log \left(\frac{\det \mathbf{F}}{\det \mathbf{F} - 1} \right) + \frac{\chi}{\det \mathbf{F}} \right] - \frac{\varepsilon \tilde{E}_K^f C_{KL}^{-1} \tilde{E}_K^f}{2 \det \mathbf{F}} \end{aligned} \quad (5.90)$$

The condition of incompressibility of the molecules yields to

$$1 + vC = \det \mathbf{F} \quad (5.91)$$

which is already embedded into the free energy function (5.90).

The derivatives in Eqs. (5.78) and (5.79) can therefore be written as

$$\begin{aligned} \frac{\partial \tilde{W}}{\partial E_{iK}} = & NkT (\delta_{iK} - C_{iK}^{-1}) - \frac{1}{2} \varepsilon \sqrt{I_3} \tilde{E}_M^f \tilde{E}_N^f [C_{iK}^{-1} C_{MN}^{-1} - 2 C_{iM}^{-1} C_{NK}^{-1}] \\ & - \frac{kT}{v} \left[\det(\mathbf{F}) \ln \frac{\det(\mathbf{F})}{\det(\mathbf{F}) - 1} - 1 - \frac{\chi}{\det(\mathbf{F})} \right] C_{iK}^{-1} \end{aligned} \quad (5.92)$$

$$\frac{\partial \tilde{W}}{\partial \tilde{E}_i^f} = -\varepsilon \det \mathbf{F} C_{iK}^{-1} \tilde{E}_K^f \quad (5.93)$$

$$\frac{\partial^2 \tilde{W}}{\partial \tilde{E}_K^f \partial \tilde{E}_L^f} = -\varepsilon \det \mathbf{F} C_{KL}^{-1} \quad (5.94)$$

$$\frac{\partial^2 \tilde{W}}{\partial \tilde{E}_i^f \partial E_{jL}} = -\varepsilon \tilde{E}_K^f \det \mathbf{F} [C_{jL}^{-1} C_{iK}^{-1} - (C_{ij}^{-1} C_{KL}^{-1} + C_{iL}^{-1} C_{Kj}^{-1})] \quad (5.95)$$

$$\begin{aligned}
 \frac{\partial^2 \tilde{W}}{\partial E_{iK} \partial E_{jL}} = & NkT \left(C_{ij}^{-1} C_{KL}^{-1} + C_{iL}^{-1} C_{Kj}^{-1} \right) \\
 & + \frac{kT}{v} \left(\det(\mathbf{F}) \ln \frac{\det(\mathbf{F})}{\det(\mathbf{F}) - 1} - 1 - \frac{\chi}{\det(\mathbf{F})} \right) \left(C_{ij}^{-1} C_{KL}^{-1} + C_{iL}^{-1} C_{Kj}^{-1} \right) \\
 & - \frac{kT}{v} \left(\det(\mathbf{F}) \ln \frac{\det(\mathbf{F})}{\det(\mathbf{F}) - 1} - \frac{\det(\mathbf{F})}{\det(\mathbf{F}) - 1} + \frac{\chi}{\det(\mathbf{F})} \right) C_{jL}^{-1} C_{iK}^{-1} \\
 & - \frac{1}{2} \varepsilon \sqrt{I_3} C_{jL}^{-1} \tilde{E}_M^f \tilde{E}_N^f \left(C_{iK}^{-1} C_{MN}^{-1} - 2C_{Mi}^{-1} C_{NK}^{-1} \right) \\
 & + \frac{1}{2} \varepsilon \sqrt{I_3} \tilde{E}_M^f \tilde{E}_N^f \left[C_{MN}^{-1} \left(C_{ij}^{-1} C_{KL}^{-1} + C_{Kj}^{-1} C_{iL}^{-1} \right) + 2C_{iK}^{-1} \left(C_{Mj}^{-1} C_{NL}^{-1} \right) \right] \\
 & - \frac{1}{2} \varepsilon \sqrt{I_3} \tilde{E}_M^f \tilde{E}_N^f \left[2C_{Mi}^{-1} \left(C_{Nj}^{-1} C_{KL}^{-1} + C_{NL}^{-1} C_{Kj}^{-1} \right) + 2C_{NK}^{-1} \left(C_{Mj}^{-1} C_{Li}^{-1} + C_{ML}^{-1} C_{ij}^{-1} \right) \right]
 \end{aligned} \tag{5.96}$$

The field equations (5.78) and (5.79) as well as (5.92) to (5.96) are solved by the UEL in ABAQUS/standard to analyze the dielectric gel immersed in the solvent and subjected to an electromechanical load. In the finite element formulation, the nominal electric field $\tilde{E}^f$, the nominal electric displacement $\tilde{D}$, and the function of free energy density $\tilde{W}$ are normalized as

$$\bar{E} = \tilde{E}^f \sqrt{\varepsilon v / kT}, \quad \bar{D} = \frac{\tilde{D}}{\sqrt{\varepsilon kT / v}}, \quad \bar{W} = \frac{\tilde{W} v}{kT} \tag{5.97}$$

The normalization results in a dimensionless parameter Nv in the free energy function, which represents the number of the monomers per polymer chain and usually ranges in $10^{-4} \sim 10^{-1}$ (Hong *et al.*, 2010).

As the first example of the dielectric gels immersed in the solvent with constraints, a layer of a gel bonded to a rigid substrate is considered, where the gel is constrained by the biaxial stretches to a fixed value, $\lambda_1 = \lambda_2 = \lambda$. A voltage is applied across the thickness of the gel, and thus the gel is free to swell or shrink in the thickness direction only. The analytical solution of the bonded gel is given by (Zhao *et al.*, 2008),

$$Nv \left(\lambda_3 - \lambda_3^{-1} \right) + \lambda^2 \left[\ln(1 - \lambda^{-2} \lambda_3^{-1}) + \lambda^{-2} \lambda_3^{-1} + \chi \lambda^{-4} \lambda_3^{-2} \right] + \frac{\bar{D}^2}{2\lambda^2} = 0 \tag{5.98}$$

where λ_3 is the stretching in the thickness direction. In the present analysis, the material parameters are given as $Nv = 10^{-3}$ and $\chi = 0.5$. Fig. 5.22 plots the nominal electric field $\bar{E}$ as a function of the nominal electric displacement $\bar{D}$ and biaxial pre-stretches λ . It is illustrated from Fig. 5.22 that the electric field $\bar{E}$ increases monotonically with the electric displacement $\bar{D}$ and decreases with the

pre-stretch λ . Fig. 5.23 shows that the thickness stretch λ_3 decreases monotonically with the electric displacement $\bar{D}$ and biaxial pre-stretches λ . The solvent content in the gel is illustrated in Fig. 5.25 as a function of the nominal electric displacement $\bar{D}$ and biaxial pre-stretches λ . The volume deformation of the gel is induced mainly by imbibing the solvent. From Figs 5.22 to 5.25, it is concluded that the larger the voltage is applied to the gel and the larger the pre-stretch is, the more the gel swells. The FEM and the analytical results are coincide with sufficient accuracy.

As the second example of the dielectric gels immersed in the solvent without constraints, the influence of the material parameter Nv is analyzed on the characteristics of the dielectric gel, where the dielectrics can swell freely in the three directions without any constraint, and a voltage is applied in one direction only, therefore, $\lambda_1 = \lambda_2 \neq \lambda_3$. The monomers per polymer chain are set at several levels, $Nv = 10^{-3}, 10^{-2}, 10^{-1}$. Fig. 5.25 demonstrates the nominal electric field $\bar{E}$ as a function of the nominal electric displacement $\bar{D}$ for different monomers Nv . It is shown from Fig. 5.25 that the electric field $\bar{E}$ increases with the increase of the monomers Nv , and the increase of the voltage induces more charges on the surfaces of the gel. Fig. 5.26 plots the deformation of gel in the thickness direction λ_3 with the electric displacement $\bar{D}$ and the number of monomers Nv , where the normal stretching λ_3 decreases with the increase of the monomers Nv , since the increase of the monomers Nv strengthens the modulus of the gel at a given temperature. Fig. 5.27 provides the biaxial stretches λ_1 with the variation of the electric displacement $\bar{D}$ and monomer Nv . With the same reason that the increase of the monomers Nv strengthens the modulus of the gel at a given temperature, the gel deforms less with the increase of monomer.

5.4. Summary

The finite element analysis is conducted for investigation of the gels and dielectrics, respectively.

The gel in the water is carried out firstly by the finite element model developed by Zhang *et al.* (2009), which is based on the field theory proposed by Hong *et al.* (2008). The finite element model is implemented by the ABAQUS through the

USER-DEFINED ELEMENT (UEL) subroutine, where the stiffness matrix and the right-hand side are coded completely. The kinetic deformations of the gels with various geometric shapes are studied in water, including the swelling of constrained gels, the free swelling of the block gels, the free swelling of the thin film of gels, and the swelling of the bonded gels, where the distributions of the stress and chemical potential in the gels are illustrated with time evolution. The swelling induces different deformation patterns, including the buckling, twisting, wrinkling, folding, and waving. Furthermore, the experiments of the free swelling of the cubic gel and the thin plate of gels are also conducted. The good agreements between the simulations and experiments are achieved. The simulations and experiments demonstrate that different geometric shapes of the gels and different constraint conditions on the gels may develop different buckling patterns.

In addition, the finite element formulation is developed for the dielectric gels, based on the field theory proposed by Suo *et al.* (2008). The present finite element formulation is able to analyze the dielectric gels subject to the electromechanical load without and within the solvent. The finite element formulation is implemented by ABAQUS/standard via its USER-ELEMENT subroutine, in order to analyze the dielectrics subject to the electromechanical load, where the layers of dielectric gels are investigated subject to electric potential only and subject to both the voltage and mechanical loads, respectively. The present finite element formulation is also employed to analyze the dielectrics immersed in a solvent with the electromechanical load, where the dielectrics with and without constraint conditions are studied. The finite element results are then compared with the analytical solutions, and the comparisons show good agreement. Therefore, the case studies demonstrate that the finite element formulation is a powerful tool for assessment of prospective applications in dielectric gels.

Fig. 5.1. The gel is subjected to the chemical and mechanical load, where the chemical load is applied by a pump to inject molecules into the gel, and the mechanical load is applied by a weight. The gel and the weight as well as the pump are coupled together to constitute the thermodynamic system, where weight and pump do work to the gel.

Fig. 5.2. A device for fluid control by gel, where the gel is constrained by the permeable rigid plate and allowed to swell in the X_1 direction only.

Fig. 5.3. The stretch ratio λ_1 (a) and the chemical potential $\bar{\mu}$ (b) evolve with time for the constrained gel swelling in the normal X_1 direction.

Fig. 5.4. A plate of gel is constrained in the thickness direction and allowed to swell in other directions, with the structure of the system (a), and the chemical potential contour in the gel at $Dt / L^2 = 0.7$ (b), $Dt / L^2 = 10$ (c), $Dt / L^2 = 100$ (d), and at the final equilibrium state (e).

(a) $t = 0$

(b) $t = 4 \text{ min}$

(c) $t = 20 \text{ h}$

Fig. 5.5. Experimental observations of a cubic gel swelling in the water at time $t = 0$ (a), $t = 4 \text{ min}$ (b), and $t = 20 \text{ h}$ (c), where the same ruler is used to measure the dimensions of the gel, with different scale levels to zoom in the wrinkles.

Fig. 5.6. Stress contours of the free swelling of a cubic gel in the water by the finite element simulation at $Dt/L^2 = 0$ (a), $Dt/L^2 = 3.75$ (b), and the equilibrium state (c).

Fig. 5.7. Stress contours of the free swelling of a cylindrical gel in the water by the finite element simulation at the dry state (a), $Dt/H^2 = 0.56$ (b), $Dt/H^2 = 1$ (c), and $Dt/H^2 = 3.75$ (d), and the equilibrium state (e).

Fig. 5.8. Chemical potential contours of the free swelling of a spherical gel in water by the finite element simulation at the dry state (a), $Dt / R^2 = 12.5$ (b), and the equilibrium state (c).

Fig. 5.9. Experimental observations of a thin plate of gel swelling in the water at the dry state (a), $t = 5 \text{ min}$ (b), and $t = 4h$ (c).

(b) $Dt/w^2 = 1$

(c) $Dt/w^2 = \infty$

Fig. 5.10. Stress contours of the free swelling of a thin plate of gel in the water by the finite element simulation at the dry state (a), $Dt/w^2 = 1$ (b), and the equilibrium state (c).

Fig. 5.11. Stress contours of the free swelling of a disk of gel in the water by the finite element simulation at the dry state (a), $Dt / R^2 = 1$ (b), $Dt / R^2 = 10$ (c), and the equilibrium state (d).

Fig. 5.12. Stress contours of the free swelling of a spherical shell of gel in the water by the finite element simulation at the dry state (a), $Dt / R^2 = 10$ (b), $Dt / R^2 = 100$ (c), and the equilibrium state (d).

Fig. 5.13. Stress contours of the swelling of a long straight strip gel fixing the both ends (a) in the water by the finite element simulation at time $Dt/h^2 = 1.8$ (b), $Dt/h^2 = 9$ (c), $Dt/h^2 = 18$ (d), and $Dt/h^2 = 180$ (e), and the equilibrium state (f).

Fig. 5.14. Stress contours of the swelling of a straight strip gel fixing a single long edge (a) in the water by the finite element simulation at time $Dt / h^2 = 1$ (b), $Dt / h^2 = 10$ (c), and the equilibrium state (d).

Fig. 5.15. Stress contours of the swelling of a straight strip gel fixing a single surface (a) in the water by the finite element simulation at time $Dt / h^2 = 10$ (b), $Dt / h^2 = 100$ (c), and the equilibrium state (d).

Fig. 5.16. Buckling patterns and the stress contours of the circular strip gel in the water by the finite element simulation, at the dry state (a), and the equilibrium state (b).

Fig. 5.17. The configuration of dielectrics under a voltage (a), and the deformation of dielectrics λ as a function of the electric field $\bar{E}$ (b).

Fig. 5.18. The configuration of a layer of dielectrics subject to the electromechanical load.

Fig. 5.19. The electric field $\bar{E}$ as a function of the stretch λ / λ_p and mechanical load P / η .

Fig. 5.20. The electric displacement $\bar{D}$ as a function of the stretch λ / λ_p and mechanical load P / η .

Fig. 5.21. The configuration of a dielectric gel in the solvent and subject to electromechanical load.

Fig. 5.22. The electric field $\bar{E}$ as a function of the electric displacement $\bar{D}$ and biaxial pre-stretches λ .

Fig. 5.23. The stretch λ_3 as a function of the electric displacement $\bar{D}$ and biaxial pre-stretches λ .

Fig. 5.24. The solvent content vC as a function of the electric displacement $\bar{D}$ and biaxial pre-stretches λ .

Fig. 5.25. The electric field $\bar{E}$ as a function of the electric displacement $\bar{D}$ and number of monomers Nv .

Fig. 5.26. The normal stretch λ_3 as a function of the electric displacement $\bar{D}$ and number of monomers Nv .

Fig. 5.27. The biaxial stretches λ_1 as a function of the electric displacement $\bar{D}$ and number of monomers Nv .

6

Conclusion and Future Work

6.1. Conclusion

The objectives achieved in this thesis are categorized into seven contributions as follows.

- Theoretical development of the multi-effect-coupling ionic-strength-stimulus (MECis) model;
- Validation of the steady-state MECis model for equilibrium swelling/shrinking behavior of the ionic-strength-sensitive hydrogels, via comparison with the experimental and other theoretical works published;
- Systematical parameter studies on the equilibrium of the ionic-strength-sensitive hydrogels by the steady-state MECis simulations, including the initial fixed charge density, the equilibrium constant, the Young's modulus, and the initial fixed charge distance;
- Examination of the MECis model for kinetic swelling/shrinking behavior of the ionic-strength-sensitive hydrogels, via comparison with the experimental works published;
- Comprehensive parameter studies on the kinetic ionic-strength-sensitive hydrogels by the transient MECis simulations, including the reversible kinetics, the initial fixed charge density, and the Young's modulus;
- Transient finite element analysis of various deformation patterns of gels in water; and
- Development of the finite element model for analysis of the dielectric gels subject to electromechanical load.

As the first contribution mentioned above, the MECis model has been developed theoretically for analysis of the chemical, electric and mechanical swelling/shrinking characteristics of the smart hydrogel responsive to different ionic strengths of the

external solution. The present model is formulated by three field equations, namely the chemical, electrical and mechanical fields, which physically result from mass conservation law, Gauss's law, and momentum conservation law, respectively. In the three fields, the constitutive equations characterize the hydrogel behavior and the interaction between the hydrogel and solution, including the constitutive flux, the fixed charge equation, and the material model of polymeric network. The constitutive flux describes the interaction between mobile ions, the fixed charge equation the interaction between mobile ions and fixed charges, and the material law the deformation pattern of the hydrogel. The three field equations associated with the constitutive models are coupled for simulation of the equilibrium and kinetic characteristics of the ionic-strength-sensitive hydrogel and the surrounding solution. Although there are many models developed for analysis of various hydrogels, the present MECis model focuses on the response of smart hydrogels to the stimulus of ionic strengths of surrounding solution, through characterization of the influence of ionic strength of the solution on the chemical, electrical and mechanical fields as well as the constitutive models. The MECis model demonstrates that the ionic strength affects the diffusion of the mobile ions, the interaction between the fixed charges and mobile ions, and the electrostatic repulsive force between the fixed charges as well as the deformation. The MECis model characterizes the swelling/shrinking process physically in several steps. Theoretically the mobile ions diffuse into or out of the hydrogel first when the hydrogel is immersed in the solution. Meanwhile, the fixed charge groups of the hydrogel start to dissociate and form an electric field. Then the electric field and the gradient of the ionic concentrations drive the mobile ions to diffuse further. The difference of the ionic concentrations over the hydrogel-solution interface results in the osmotic pressure, which drives the hydrogel to swell or shrink. At the same time, the electrostatic force between the fixed charges also contributes to expansion of the hydrogel. The swelling or shrinking of the hydrogel results in the redistributions of the ionic concentrations and fixed charge groups as well as electric field. This reformulates the chemical, electrical and mechanical coupled fields, and drives the mobile ions to diffuse, and makes the hydrogel deform further until the system reaches an equilibrium state.

The second contribution extracted from the present thesis is the validation of the steady-state MECis model for equilibrium swelling/shrinking behavior of the ionic-strength-sensitive hydrogels, via comparison with the experimental and other

theoretical works published previously. The equilibrium swelling and shrinking of PAAP, PAI, PAAS and PAMC hydrogels are studied using the present MECis model. The four types of hydrogels include different properties of the ionic-strength-sensitive hydrogel. For example, they dissociate either weakly (PAAP, PAI) or strongly (PAAS, PAMC) in solution, and their dimensions are from 4 to 18 mm. The initial fixed charge density also ranges from low (47mM) to high (3459mM) levels. Their mechanical strengths range from 0.008 to 1MPa. The simulation results are compared with the corresponding experiments, and achieve a good agreement. The present MECis model is also compared with other theories, including the modified Flory-Rehner theory-I and -II, and the gel-swelling model. The comparison demonstrates that the present model provide a more accurate prediction by considering more environmental physical and chemical conditions. It is therefore concluded that the present MECis model is a good tool to simulate the equilibrium of the ionic-strength-sensitive hydrogel, and it provides a theoretical way for analysis of the equilibrium of the smart hydrogel, which is much time and cost saving compared with experimental studies.

The systematical parametric studies for the equilibrium of the ionic-strength-sensitive hydrogels using the steady-state MECis simulations are carried out as the third contribution, in order to understand further how the environmental condition as well as physical and chemical parameters influence the equilibrium behavior of the hydrogel. The four parameter studies are exemplified in this thesis, including the influences of the initial fixed charge density, the equilibrium constant, the Young's modulus, and the initial fixed charge distance on the equilibrium swelling/shrinking characteristics. Accordingly, the influence of the four parameters on the swelling ratio, the chemical, electrical, and mechanical fields is investigated, where the distributions of several important field variables are analyzed in details, including the fixed charge density, the ionic concentration, the electric potential, and the displacement. It is concluded that the swelling ratio decreases with the decrease of the initial fixed charge density, and the increase of the equilibrium constant, the Young's modulus as well as the initial fixed charge distance.

As the fourth contribution from the thesis, the examination of the transient MECis model for kinetic swelling/shrinking behavior of the ionic-strength-sensitive hydrogel is achieved via comparison with the experimental work published previously. The kinetics of the swelling/shrinking and/or reversible properties of the HMDT, CPMA, SMA and HEMA-VBT hydrogels is simulated by the transient MECis model, and

compared with the corresponding experiments, in order to theoretically trace the behavior of the hydrogels evolving with time. The four types of hydrogels represent the different properties of the ionic-strength-sensitive hydrogels, namely, from low to high Young's modulus, from small to large fixed charge density, from low to high equilibrium constant. The four studies also cover the kinetic swelling, shrinking and reversible behaviors of the ionic-strength-sensitive hydrogel. It is thus concluded that the MECis model is capable of modeling and simulation of the kinetics of the ionic-strength-sensitive hydrogels well.

The comprehensive parametric studies of the kinetic ionic-strength-sensitive hydrogels with transient MECis simulations are accomplished as the fifth contribution, where the reversible kinetics, the influence of the initial fixed charge density and Young's modulus on the kinetics of the ionic-strength-sensitive hydrogel are studied in details. The kinetics of swelling ratio with different parameters, the kinetic distributions of the significant field variables, including the fixed charge density, the ionic concentration, the electric potential, and the displacement, are analyzed in details. It is concluded that the present MECis model provides a powerful and convenient tool for studying the influence of the various parameters on the kinetic characteristics, while almost impossible to be investigated experimentally.

The sixth contribution comes from the transient finite element analysis of the deformation patterns of the gels in water, where the kinetic deformation of the gels with various shapes and constraints in water are studied, including the constrained gels, the block gels, the thin film of gels, and the bonded gels. The different deformation patterns are achieved, including the buckling, twisting, wrinkling, folding and waving. By the finite element simulation, the distributions of stress and chemical potential in the gels are illustrated and discussed in details with time evolution. The experiments are also carried out to observe the swelling and wrinkling of the cubic and thin film gels. The finite element simulations are compared with the experiments, and a good agreement is obtained. It is concluded that the gel in water can develop different wrinkling patterns. For free swelling gels, they can recover back to the original shape with much larger volume change at final equilibrium.

The last contribution from the present thesis is the development of the finite element formulation for the dielectrics based on the existing field theory. The formulation is implemented by the ABAQUS through the USER-DEFINED

ELEMENT (UEL) subroutine, where the stiffness matrix $\mathbf{A}^{t+\Delta t}$ and the right hand side vector $\mathbf{Y}^{t+\Delta t}$ of Eqn. (5.47) are coded completely. The finite element formulation is employed to analyze the deformation of the dielectric gels subject to electromechanical load, and for analysis of the dielectric gels in the solvent with electromechanical load. The finite element results are then compared with the analytical solution, and it is thus concluded that the finite element formulation provides an effective tool for analysis of dielectric gels within or without the solvent.

In conclusion, the seven contributions mentioned above constitute the entire thesis. It is believed that the present research work is significant in science for further understanding of fundamental theoretical mechanism of the ionic-strength-sensitive hydrogel, and useful in bioengineering to assist the design and optimization of the hydrogel-based BioMEMS devices.

6.2. Future Work

Due to the complexity of the hydrogel-solution system, the modeling and simulation still have a long way to go. In this section, several possible interesting studies are recommended below for future work.

One of the future studies may focus on the improvement of constitutive relations in the present MECis model for the ionic-strength-sensitive hydrogel. As mentioned above, the MECis model is a theoretical framework for simulation of the ionic-strength-sensitive hydrogel including the chemical, electrical and mechanical coupled effects together, where the constitutive models demonstrate the fundamental characteristics of the hydrogel. It is possible to further consider several more effects on the constitutive behaviors in the MECis model. For example, the influence of the pore size of the polymeric network on constitutive flux may be considered, where the larger the pore size is, the faster the diffusion rate is. The environmental temperature is also an important effect to be considered on the equilibrium reaction between the fixed charges and the mobile ions. The temperature may influence the reaction rate, and therefore give a non-static fixed charge equation, which further results in a non-static electric field equation. Another recommended work is on the diffusion coefficients of the mobile ions, which may be related to the properties of the hydrogel, including the length of the polymeric chain, the hydrogel density, and the fixed charge properties.

The effort of the future work may also be made on the more precise description of

the material laws of the ionic-strength-sensitive hydrogel, apart from the elastic theory in the MECis model. Other material laws may account for more accurate behaviors of the smart hydrogel, such as the plasticity, viscoelasticity and viscoplasticity of the hydrogel. It is also possible to integrate the hyperelasticity material model from thermodynamics and statistic mechanics into the MECis model, like the Flory-Rehner model.

The development of the theoretical models for the hydrogels responding to other environmental stimuli is a more interesting work for the future, such as the electric-, magnetic- and photonic-sensitive hydrogels, which usually possess fast response property and can thus be used in numerous bioengineering fields. The fundamental mechanism of the deformation of the smart hydrogel subject to electric, magnetic and photonic fields may be explained simply by the interaction between the particles, such as electrons, atoms, and protons, such that the difficulties for the theoretical development may come from the formulation of the forces between the particles. A possible approach to avoid this problem may be the use of the virtual work principle, where the field formations can be defined directly.

The development of the mathematical model for the hydrogels responding to the coupled stimuli is a possible research direction in the future, for example, the pH-temperature-sensitive hydrogel, the pH-thermo-ionic-strength-sensitive hydrogel, the pH-ionic-strength-sensitive hydrogel, and the electric-ionic-strength-sensitive hydrogel. The material property responsive to the coupled stimuli may be not simply induced by the linear addition of the two stimuli. They may affect each other, and this increases the difficulties for understanding of the stimulus and responsive characteristics.

Another important future work may attribute to the development of the model for the nano-scale phenomena of the gel for nano-applications, such as nanogenerators and nanopiezotronics, which can convert the mechanical energy, acoustic/ultrasonic vibration energy, and biofluid hydraulic energy into electric energy, in contrast to the present hydrogel with the mechanical deformation induced by the stimuli. Let us take a simple theory developed by Wang (2008) as example, where the mechanical and electric fields are presented by the classical mechanical equilibrium and Gaussian equations,

$$\frac{\partial \sigma_{ij}}{\partial x_i} = 0 \quad (5.99)$$

$$\frac{\partial D_i}{\partial x_i} = 0 \quad (5.100)$$

where $\boldsymbol{\sigma}(\boldsymbol{\varepsilon}, \mathbf{E}^f, \mathbf{D})$ is the stress tensor associated with the strain $\boldsymbol{\varepsilon}$, the electric field $\mathbf{E}^f$, and the electric displacement $\mathbf{D}$. The constitutive equations are given as

$$\sigma_i = c_{ij}\varepsilon_j - e_{ki}E_k^f \quad (5.101)$$

$$D_i = e_{ij}\varepsilon_j + \kappa_{ik}E_k^f \quad (5.102)$$

where σ_i and ε_i are the principal stress and strain, c_{ij} is the linear elastic constant, e_{ij} is the linear piezoelectric coefficient, and κ_{ij} is the dielectric constant. The strain ε_i is required to satisfy the compatibility condition. The above linear theory (5.99)-(5.102) was applied to a laterally bent piezoelectric (Wang, 2008). The future work may be suggested to extend the theory to nonlinear behavior and other deformation patterns of the piezotronic, since the nanogenerators have the exciting applications in electronics, optoelectronics, sensors and the biological sciences. It is also possible to develop the model for the dynamic behavior of the concurrently deformation and the generation of the electric potential.

The future study may also be recommended on the two- or three-dimensional simulations of the ionic-strength-sensitive hydrogel, since the one-dimensional analysis of the MECis model is conducted only in the present thesis. The 2-D or 3-D geometry may have different swelling/shrinking behaviors, which can be addressed by the simulation. Furthermore, the arbitrary Lagrangia-Eulearian (ALE) method could be employed, which combines the best features of both the Lagrangian and the Eulerian approaches, in order to better simulate the interaction between the solution and hydrogel with large deformation. In the ALE method, the nodes of the computational mesh may be moved with the hydrogel and solution in normal Lagrangian fashion, or be fixed in Eulerian manner, or be moved in an arbitrarily specified way to give a continuous rezoning capability. Due to the freedom in moving the computational mesh offered by the ALE method, the greater distortions of the hydrogel can be caught up better.

Another possible future work is to couple the fluid and solid dynamics to model

the hydrogel in a fluid flow. In order to model the behavior more realistically, it is possible to consider how the fluid flow in the solution influences the swelling/shrinking characteristics of the hydrogel. The fluid flow may be governed by the fluid dynamics and the solid network of the hydrogel by the solid dynamics, where the fluid flow, the ionic diffusion, the charge, and the network deformation are all coupled together. The way for coupling may be a key and significantly difficult. The difficulty may also arise from the interaction between the fluid flow and the hydrogel structure.

It is proposed to develop more efficiently numerical scheme for solving the system of PDEs as a future work, since the coupled nonlinear partial differential equations with moving boundary and local high gradient in the MECis model are difficult to be solved. The numerical method should be able to capture the high gradient and jump over the hydrogel-solution interface.

The finite element analysis of the gel in the water could be extended to more complicated geometry in future work. In addition, the material model in the finite element analysis could also be improved or refined. The present Flory-Rehner theory, which is based on the thermodynamics and statistical mechanics, is derived mainly from the microscopic behaviors of the solvent molecules and polymer chains. It is highly simplified and based on an idea circumstance. The improvement may be put on the consideration of more realistic circumstance.

The development of the numerical method for the electromechanical instability of dielectric gels is also a future research direction. The electromechanical instability occurs when the applied force and the voltage reach the critical conditions, which is observed and investigated analytically (Zhao and Suo, 2009). However, it is still a challenge to catch up the electromechanical instability numerically, although the Riks method was applied widely for the analysis of the structural instability. Therefore, it is recommended to improve the Riks method for the analysis of the electromechanical instability.

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Publications Arising from the Thesis

Journal Papers

1. **Fukun Lai** and Hua Li. Modeling of effect of initial fixed charge density on smart hydrogel response to ionic strength of environmental solution. *Soft Matter*, 2010, 6(2), 311-320.
2. **Fukun Lai** and Hua Li. Transient modeling for kinetics swelling/deswelling of the ionic-strength-sensitive hydrogel. *The European Physical Journal E: Soft Matter and Biological Physics*, 2010, 31(3), 269-274.
3. **Fukun Lai**, Hua Li and Rongmo Luo. Chemo-electro-mechanical modeling of ionic-strength-sensitive hydrogel: Influence of Young's modulus. *International Journal of Solids and Structures*, 2010, 47(22-23), 3141-3149.
4. Hua Li and **Fukun Lai**. Multiphysics modeling of responsive characteristics of ionic-strength-sensitive hydrogel. *Biomedical Microdevices*, 2010 12(3), 419-434.
5. Hua Li, **Fukun Lai** and Rongmo Luo. Analysis of responsive characteristics of ionic-strength-sensitive hydrogel with consideration of effect of equilibrium constant by a chemo-electro-mechanical model. *Langmuir*, 2009 25(22), 13142-13150.
6. Hua Li and **Fukun Lai**. Transient analysis of the effect of the initial fixed charge density on the kinetic characteristics of the ionic-strength-sensitive hydrogel by a multi-effect-coupling model. *Analytical and Bioanalytical Chemistry*, 2011 399(3), 1233-1243.
7. **Fukun Lai** and Hua Li. Transient modeling of the reversible response of the hydrogel to the change in the ionic strength of solutions. *Mechanics of Materials*, 2011 43(6), 287-298.
8. Hua Li and **Fukun Lai**. Analysis of the kinetics of shrinking of the ionic-strength-sensitive hydrogel with a multi-physical model. *International*

Journal of Applied Mechanics, 2011 3(2), 313-334.

9. Hua Li and **Fukun Lai**. Modeling of ionic-strength-sensitive hydrogel: Effect of initial distance between fixed charge. *Soft Materials* (in press).
10. **Fukun Lai** and Hua Li. Analysis of the kinetics deformation of ionic-strength-sensitive hydrogel with different Young's moduli by a chemo-electro-mechanical model. *Physical Review E* (submitted).

Conference Papers

1. **Fukun Lai** and Hua Li. A chemo-electro-mechanical model for simulation of ionic-strength-sensitive hydrogel. *The 4th International Conference on Advanced Computational Engineering and Experimenting 2010 (ACE-X 2010), Paris*.
2. **Fukun Lai** and Hua Li. A continuum theory for simulation of ionic-strength-sensitive hydrogel for BioMEMS application. *International Conference on Materials for Advanced Technologies 2009 (ICMAT 2009), Singapore*.

Appendix A: Notations and Rules

In this thesis, the tensor and vector are written either in the bold or indicial form. For example, a vector $\mathbf{a}$ in an indicial form is written as

$$\mathbf{a} = a_I \quad I = 1, \dots, n \quad (\text{A.1})$$

where I is the index from 1 to n . Its corresponding matrix form is

$$\mathbf{a} = [a_1, \dots, a_n]^T \quad (\text{A.2})$$

A second-order tensor is denoted as

$$\mathbf{A} = A_{IJ}, \quad I, J = 1, \dots, n \quad (\text{A.3})$$

which represents a matrix form as

$$\mathbf{A} = \begin{bmatrix} A_{11} & \cdots & A_{1n} \\ \vdots & \ddots & \vdots \\ A_{n1} & \cdots & A_{nn} \end{bmatrix} \quad (\text{A.4})$$

The matrix and indicial forms are equivalent mathematically for a tensor. However, the indicial form is much compact.

The dot product of the tensors in the indicial form imposes an important convention, named summation convention. It is stated that a summation over this index is implied if the index is repeated twice in a term. For example, the product of two vectors is given as

$$\mathbf{a} \cdot \mathbf{b} = a_I b_I = a_1 b_1 + a_2 b_2 + a_3 b_3 \quad (\text{A.5})$$

where the repeated I in the term indicates that the results of the three multiplications should be added.

The matrix-matrix multiplication follows in a similar manner

$$D_{IJ} = A_{IK} B_{KJ} \quad (\text{A.6})$$

where the repeated index K is summed over. The repeated index in a term is called the dummy index since it is summed over, and it can be replaced by any index. In

contrast, it is called the free index if an index is not repeated.

The gradient of a scalar function is represented in indicial form as

$$g_I = f_{,I} = \frac{\partial f}{\partial x_I} \quad (\text{A.7})$$

where the component of the coordinate system is denoted by x_I . The comma in the indicial notation indicates the derivative of f with respect to each coordinate x_I .

The divergence of a vector is denoted as

$$h = g_{I,I} = \frac{\partial g_I}{\partial x_I} \quad (\text{A.8})$$

where the repeated index I is summed over and results in a scalar.

The gradient of a vector function is a second-order tensor and defined as

$$g_{I,J} = \frac{\partial g_I}{\partial x_J} \quad (\text{A.9})$$

The Kronecker delta function plays an essential role in indicial notation and tensor algebra. It is defined as

$$\delta_{IJ} = \begin{cases} 1 & I = J \\ 0 & I \neq J \end{cases} \quad (\text{A.10})$$

It is equal to the unit second-order tensor. If two matrices satisfy

$$A_{IK} B_{KJ} = \delta_{IJ} \quad (\text{A.11})$$

then A_{IK} is the inverse of B_{KJ} .

Appendix B:

Hermite-Cloud Method

The Hermite-cloud method was developed by the combination of the Hermite theorem and the point collocation, where the Hermite theorem is applied to construct the interpolation functions, and the point collocation to discretize the partial differential equations (PDEs). The present numerical technique is based on the idea of the classical reproducing kernel particle method (RKPM).

The main characteristic of the reproducing kernel method is able to reproduce the unknown function by integration transform over the domain. Taking a 2D unknown real function $f(x, y)$ in a domain Ω as an example. The approximation $f^h(x, y)$ of the real function is reproduced by the window function $\Phi(x - p, y - q)$ as

$$f^h(x, y) = \int_{\Omega} \Phi(x - p, y - q) f(p, q) dp dq \quad (\text{B.1})$$

An ideal window function should be orthogonal, and its integration over the domain Ω should be unity, in order to exactly reproduce the real function.

Following the idea of the classical RKPM, the window function could be constructed by a correction function $C(x, y, p, q)$ and a kernel function $K(x - p, y - q)$ as

$$\Phi(x - p, y - q) = C(x, y, p, q) K(x - p, y - q) \quad (\text{B.2})$$

If a fixed kernel technique centered at the point (x_k, y_k) is applied, the approximate function can be rewritten as

$$f^h(x, y) = \int_{\Omega} C(x, y, p, q) K(x_k - p, y_k - q) f(p, q) dp dq \quad (\text{B.3})$$

The kernel function may be constructed in different forms of weighted window functions, depending on the problems. In the Hermite-cloud method, a form of cubic spline function is employed as

$$K(x_k - p, y_k - q) = \frac{1}{(\Delta x \Delta y)} W^*\left(\frac{x_k - p}{\Delta x}\right) W^*\left(\frac{y_k - q}{\Delta y}\right) \quad (\text{B.4})$$

where $W^*(z)$ is a cubic-spline window function and is given as

$$W^*(z) = \begin{cases} 0 & |z| \geq 2 \\ \frac{(2 - |z|)^3}{6} & 1 \leq |z| \leq 2 \\ \frac{2}{3} - z^2 \left(1 - \frac{|z|}{2}\right) & |z| \leq 1 \end{cases} \quad (\text{B.5})$$

where $z = (x_k - p) / \Delta x$ or $z = (y_k - q) / \Delta y$ for x or y direction respectively. Δx and Δy denote the cloud sizes of the fixed kernel point (x_k, y_k) , and are adjustable according to the accuracy requirement.

The correction function $C(x, y, p, q)$ can be expressed as a sum of linearly independent basis functions. The selection of the basis functions is based mainly on the highest-order derivative term of the governing PDE. Here the correction function is represented by a product of the β th basis function vector $\mathbf{B}(p, q)$ and the β th coefficient vector $\mathbf{C}^*(x, y)$,

$$C(x, y, p, q) = \mathbf{B}(p, q) \mathbf{C}^*(x, y) \quad (\text{B.6})$$

For a two-dimensional second-order PDE system, the basis function can be given as

$$\mathbf{B}(p, q) = \{b_1(p, q), b_2(p, q), \dots, b_\beta(p, q)\} = \{1, p, q, p^2, pq, q^2\} \quad (\text{B.7})$$

and the corresponding correction function coefficient as

$$\mathbf{C}^{*T}(x, y) = \{c_1, c_2, \dots, c_\beta\} \quad (\text{B.8})$$

where c_i is the unknown coefficient and it can be determined by the consistency conditions

$$b_i(x, y) = \int_{\Omega} \mathbf{B}(p, q) \mathbf{C}^*(x, y) K(x_k - p, y_k - q) b_i(p, q) dp dq \quad (i = 1, 2, \dots, \beta) \quad (\text{B.9})$$

By the point collocation technique, the consistency conditions can be rewritten in discrete form as

$$b_i(x, y) = \sum_{n=1}^{N_T} \mathbf{B}(p_n, q_n) \mathbf{C}^*(x, y) K(x_k - p_n, y_k - q_n) b_i(p_n, q_n) \Delta S_n \quad (\text{B.10})$$

where N_T is the number of total points sprinkled over both the interior computational domain Ω and along its edges. The subscript n denotes the n th point in the domain, and ΔS_n is the cloud area associated with the n th point.

Rewriting (B.10) in matrix form gives

$$\mathbf{B}^T(x, y) = \mathbf{A}(x_k, y_k) \mathbf{C}^*(x, y) \quad (\text{B.11})$$

where $\mathbf{A}$ is the known symmetric matrix associated with the fixed kernel, and it is obtained by

$$A_{ij}(x_k, y_k) = \sum_{n=1}^{N_T} b_i(p_n, q_n) K(x_k - p_n, y_k - q_n) b_j(p_n, q_n) \Delta S_n \quad (\text{B.12})$$

The unknown coefficient $\mathbf{C}^*$ can thus be expressed explicitly as

$$\mathbf{C}^*(x, y) = \mathbf{A}^{-1}(x_k, y_k) \mathbf{B}^T(x, y) \quad (\text{B.13})$$

By substituting Eqn. (B.13) into $C(x, y, p, q) = \mathbf{B}(p, q) \mathbf{C}^*(x, y)$, the approximation $f^h(x, y)$ of the unknown real function $f(x, y)$ can be obtained in the following discrete form,

$$\begin{aligned} f^h(x, y) &= \sum_{n=1}^{N_T} (\mathbf{B}(p_n, q_n) \mathbf{A}^{-1}(x_k, y_k) \mathbf{B}^T(x, y) K(x_k - p_n, y_k - q_n) \Delta S_n) f_n \\ &= \sum_{n=1}^{N_T} N_n(x, y) f_n \end{aligned} \quad (\text{B.14})$$

where f_n is the unknown point value at the n th point, and $N_n(x, y)$ is the shape functions defined as,

$$N_n(x, y) = \mathbf{B}(p_n, q_n) \mathbf{A}^{-1}(x_k, y_k) \mathbf{B}^T(x, y) K(x_k - p_n, y_k - q_n) \Delta S_n \quad (\text{B.15})$$

The first-order derivatives of the unknown function $f(x, y)$ with respect to the independent variables x and y are written as

$$g_x = \frac{\partial f}{\partial x}, \quad g_y = \frac{\partial f}{\partial y}, \quad (\text{B.16})$$

The functions $g_x(x, y)$ and $g_y(x, y)$ are considered as additional unknown functions and discretized by Eqn. (B.14) in a similar manner. Therefore, their approximations can be written as

$$g_x^h(x, y) = \sum_{m=1}^{N_s} M_m(x, y) g_{xm}, \quad g_y^h(x, y) = \sum_{m=1}^{N_s} M_m(x, y) g_{ym} \quad (\text{B.17})$$

where $N_S(\leq N_T)$ is the number of total points covering the domain, g_{xm} and g_{ym} denote the unknown point values at the m th point. $M_m(x, y)$ is the shape function associated with the first-order differential functions of $f^h(x, y)$.

In order to satisfy the consistency condition, the shape function should have the following properties

$$1.0 = \sum_{n=1}^{N_T} N_n(x, y) \quad (\text{B.18})$$

$$x = \sum_{n=1}^{N_T} N_n(x, y) x_n \quad (\text{B.19})$$

$$y = \sum_{n=1}^{N_T} N_n(x, y) y_n \quad (\text{B.20})$$

According to the Hermite interpolation theorem, a meshless approximation $f^h(x, y)$ of the unknown real function $f(x, y)$ can now be constructed as

$$\begin{aligned} f^h(x, y) = & \sum_{n=1}^{N_T} N_n(x, y) f_n + \sum_{m=1}^{N_S} \left(x - \sum_{n=1}^{N_T} N_n(x, y) x_n \right) M_m(x, y) g_{xm} + \\ & \sum_{m=1}^{N_S} \left(y - \sum_{n=1}^{N_T} N_n(x, y) y_n \right) M_m(x, y) g_{ym} \end{aligned} \quad (\text{B.21})$$

Due to the additional unknown functions g_x and g_y , it is necessary to impose auxiliary conditions to formulate a complete set of PDEs. The auxiliary conditions are developed naturally by imposing the first-order partial derivative with respect to the indicated spatial variable on the approximate solution $f^h(x, y)$. By considering Eqs. (B.18) to (B.20), the auxiliary conditions are derived as,

$$\begin{aligned} & \sum_{n=1}^{N_T} N_{n,x}(x, y) f_n - \sum_{m=1}^{N_S} \left(\sum_{n=1}^{N_T} (N_{n,x}(x, y) x_n) \right) M_m(x, y) g_{xm} \\ & - \sum_{m=1}^{N_S} \left(\sum_{n=1}^{N_T} (N_{n,x}(x, y) y_n) \right) M_m(x, y) g_{ym} = 0 \end{aligned} \quad (\text{B.22})$$

$$\begin{aligned} & \sum_{n=1}^{N_T} N_{n,y}(x, y) f_n - \sum_{m=1}^{N_S} \left(\sum_{n=1}^{N_T} (N_{n,y}(x, y) y_n) \right) M_m(x, y) g_{ym} \\ & - \sum_{m=1}^{N_S} \left(\sum_{n=1}^{N_T} (N_{n,y}(x, y) x_n) \right) M_m(x, y) g_{xm} = 0 \end{aligned} \quad (\text{B.23})$$

In order to implement the Hermite-cloud method in partial differential boundary

value (PDBV) problems, a general form is presented as

$$\begin{aligned} Lf(x, y) &= P(x, y) & \text{in } \Omega \\ f(x, y) &= Q(x, y) & \text{in } \Gamma_D \\ \partial f / \partial n &= R(x, y) & \text{in } \Gamma_N \end{aligned} \quad (\text{B.24})$$

where L is the differential operator, $f(x, y)$ an unknown real function, Ω the interior domain of the problem, Γ_D the section of the boundary where Dirichlet boundary conditions are imposed, and Γ_N the section of the boundary where Neumann boundary conditions are involved. By means of the point collocation technique, the PDBV equations are discretized as

$$\begin{aligned} \mathbf{L}f^h(x_i, y_i) &= P(x_i, y_i) & i = 1, 2, \dots, N_\Omega \\ f^h(x_i, y_i) &= Q(x_i, y_i) & i = 1, 2, \dots, N_D \\ f_{,n}^h &= R(x_i, y_i) & i = 1, 2, \dots, N_N \end{aligned} \quad (\text{B.25})$$

where N_Ω , N_D and N_N are the numbers of scattered points in the interior computational domain, and along the Dirichlet and Neumann edges of the domain, respectively. The number of totally scattered points is thus $N_T = N_\Omega + N_D + N_N$.

Substituting the approximations (B.17) and (B.21) into the Eqn. (B.25), a complete set of discretized equations is constructed for the PDBV problem with the auxiliary conditions. By rearrangement, a set of discrete algebraic equations with respect to the unknown point values f_i , g_{xi} and g_{yi} is obtained as

$$[H_{ij}]_{(N_T+2N_S) \times (N_T+2N_S)} \{F_i\}_{(N_T+2N_S) \times 1} = \{d_i\}_{(N_T+2N_S) \times 1} \quad (\text{B.26})$$

where $\{d_i\}$ and $\{F_i\}$ are $(N_T + 2N_S)$ th order vectors,

$$\{F_i\}_{(N_T+2N_S) \times 1} = \{\{f_i\}_{1 \times N_T}, \{g_{xi}\}_{1 \times N_S}, \{g_{yi}\}_{1 \times N_S}\}^T \quad (\text{B.27})$$

$$\{d_i\}_{(N_T+2N_S) \times 1} = \{\{P(x_i, y_i)\}_{1 \times N_\Omega}, \{Q(x_i, y_i)\}_{1 \times N_D}, \{R(x_i, y_i)\}_{1 \times N_N}, \{0\}_{1 \times 2N_S}\}^T \quad (\text{B.28})$$

and $[H_{ij}]$ is a $(N_T + 2N_S) \times (N_T + 2N_S)$ coefficient matrix

$$[H_{ij}] = \begin{bmatrix}
 [\mathbf{L}N_j(x_i, y_i)]_{N_\Omega \times N_T} & [\mathbf{L}(x_i - \sum_{n=1}^{N_T} N_n(x_i, y_i)x_n)M_j(x_i, y_i)]_{N_\Omega \times N_S} & [\mathbf{L}(y_i - \sum_{n=1}^{N_T} N_n(x_i, y_i)y_n)M_j(x_i, y_i)]_{N_\Omega \times N_S} \\
 [N_j(x_i, y_i)]_{N_D \times N_T} & [0]_{N_D \times N_S} & [0]_{N_D \times N_S} \\
 [0]_{N_N \times N_T} & [M_j(x_i, y_i)]_{N_N \times N_S} & [M_j(x_i, y_i)]_{N_N \times N_S} \\
 [N_{j,x}(x_i, y_i)]_{N_S \times N_T} & [-\sum_{n=1}^{N_T} N_{n,x}(x_i, y_i)x_n)M_j(x_i, y_i)]_{N_S \times N_S} & [-\sum_{n=1}^{N_T} N_{n,x}(x_i, y_i)y_n)M_j(x_i, y_i)]_{N_S \times N_S} \\
 [N_{j,y}(x_i, y_i)]_{N_S \times N_T} & [-\sum_{n=1}^{N_T} N_{n,y}(x_i, y_i)x_n)M_j(x_i, y_i)]_{N_S \times N_S} & [-\sum_{n=1}^{N_T} N_{n,y}(x_i, y_i)y_n)M_j(x_i, y_i)]_{N_S \times N_S}
 \end{bmatrix}$$

(B.29)

The above complete set of linear algebraic equations can be solved to obtain $(N_T + 2N_S)$ point values for $\{F_i\}$. Accordingly, the approximate solutions $f^h(x, y)$ of the PDBV problem and the corresponding first-order differentials $g_x^h(x, y)$ and $g_y^h(x, y)$ can be computed.